Journal of Archaeological Science 50 (2014) 288–304

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

Glassy faience from the Hallstatt C period in Poland: a chemico-physical study

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ARTICLE INFO

Article history:
Received 14 March 2014
Received in revised form
25 June 2014
Accepted 27 June 2014
Available online 29 July 2014

Keywords:
Glassy faience
Glass
Beads
Hallstatt period
Poland
LA-ICPMS
EPMA

ABSTRACT

Beads and pin heads made of *glassy faience*, often decorated with true *glass*, discovered at seven different cemetery sites in Poland and dated chiefly to the Hallstatt C period (c. 750/700–600 BC), were examined by the LA-ICPMS and EPMA methods. The analysis involved 48 samples from 39 objects. The main objectives were: (i) to characterize the glassy faience in terms of the physical structure and chemical composition of the glass; (ii) to evaluate differences in the chemical composition of the glass forming the glassy faience; (iii) to examine the chemical composition of the true glass in the decoration on objects made of glassy faience. Glassy faience was found to be made of glass and numerous quartz grains, inclusions and gas bubbles. Manifest in the true glass of the decoration were numerous minor inclusions of the colorant, represented mostly by a compound of lead and antimony. Two groups of glass forming glassy faience were distinguished based on the differences in chemical composition: LMMK and LMG_{GF}. The first is characterized by a moderate concentration of K_2O (average 2.7%), high Al_2O_3, Fe_2O_3 and some trace elements (e.g. B and Ti). The second has a generally lower content, compared to LMMK, of K_2O, Na_2O, Al_2O_3, Fe_2O_3, B_2O_3 and TiO_2, but higher PbO and Sb_2O_5. True glass LMG contained little K_2O, Al_2O_3, B_2O_3 and TiO_2, but a large amount of PbO and Sb_2O_5. All of the glasses had a low content of CaO and MgO. LMMK glass was melted using sand and a flux that could not be easily identified (plant ash?), whereas LMG_{GF} and LMG glass used sand and natron. The glassy faience is usually blue and was colored with cobalt compounds. The yellow glass of the decoration was colored with lead antimonate.

1. Introduction

Glassy materials from Bronze Age Europe can be subdivided into *faience*, *glassy faience* and true *glass* (cf. Santropadre and Verità, 2000; Angelini et al., 2004). The physical structure, meaning the quantitative proportions between glass and unreacted crystalline grains (most often quartz) or newly formed grains and crystals, is the classification criterion. A similar division can be applied to glassy materials from the Early Iron Age from excavations in modern Poland.

Physico-chemical analyses of glassy materials from the Hallstatt C–D phase (c. 750/700–450/400 BC) found in Poland have demonstrated to date the presence of high magnesium glass (HMG) and, more frequently, low magnesium glass (LMG) (Purowski, 2010, 2012; Purowski et al., 2012). The former most often has a relatively high concentration of K_2O and MgO. It is assumed that the soda used in HMG melting came from halophyte plant ash. HMG glass may have first appeared in Mesopotamia at the end of the 3rd millennium BC, but production on a larger scale did not start until about the 16th century BC (Henderson, 1989, 2000; Towle et al., 2001; Gratuze and Billaud, 2003; Nikita and Henderson, 2006). Glasses of this kind are typical of the workshops of Egypt, Mesopotamia, Anatolia, Mycenaean Greece, southwestern Iran and central Asia. They have also been discovered in Europe in archaeological sites from the Bronze and Early Iron Ages (Henderson, 1989; Purowski et al., 2012) and in Eastern Europe in as late as 4th–3rd century BC contexts (Galibin, 2001: 124–125). About the 9th or 8th century BC, HMG glass started to be replaced with LMG glass, which has a low content of K_2O and MgO. It is assumed that the glass was made with mineral soda, such as natron. LMG glass is known from Mesopotamia, Greece and Egypt. In Europe, it is found starting from the Early Iron Age (e.g.

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http://dx.doi.org/10.1016/j.jas.2014.06.022
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Braun, 1983; Henderson, 1989, 2000; Gratuze and Billaud, 2003; Nikita and Henderson, 2006; Arletti et al., 2010; Purowski et al., 2012).

Research on glassy materials found in Poland has demonstrated that in the Hallstatt C (c. 750/700–600 BC) and perhaps still at the very beginning of Hallstatt D, glasses had low magnesium and medium potassium (LMMK) contents (Purowski, 2010, 2012; Purowski et al., 2012). They contained numerous unreacted grains of quartz and other inclusions (Purowski et al., 2012: Fig. 8). According to the classifications proposed by some researchers (cf. Santropadre and Verità, 2000; Angelini et al., 2004), they should be considered not so much as true glass, but as glassy faience, a *transitional* material between glass and faience (Henderson, 2013: 15).

Beads made of glassy faience were produced in a similar way to glass beads from the Bronze and Early Iron Ages, by the winding technique. Traces of technical processes (such as an unmelted side or end of a glass thread) apparent on some objects from Poland attest to the use of this production technique (Purowski, 2012: Fig. 22). It will be recalled that the winding technique has the glassmaker winding the glass mass onto a heated metal rod (e.g. Van der Sleen, 1967; Purowski, 2007). Faience beads were made in a different way, essentially forming first the body by modeling the damp quartz paste by hand or pressing the paste into open-faced moulds, and then glazing. Three different glazing techniques were used, namely application, efflorescence and cementation (e.g. Tite and Bimson, 1986; Tite and Shortland, 2003; Nicholson and Peltenburg, 2000).

To date, the material of most examples of glassy faience discovered in Poland has been analyzed solely by EPMA; only a few objects have been examined by LA-ICPMS, which identifies both major and trace elements (Purowski et al., 2012). Therefore, to determine a more complete chemical composition of the glassy faience, it was essential to conduct further lab analyses.

The objectives of the present article are: (i) to characterize glassy faience in terms of the physical structure and chemical composition of the glass; (ii) to indicate differences in chemical composition of the glass forming glassy faience; (iii) to determine the chemical composition of the glass in the decoration on objects made of glassy faience.

Table 1
Description of studied samples (abbreviations: a = glass of the matrix; b = glass of the ornament; Ha = Hallstatt).

Site	Sample no.	Object category	Chronology	Colour of glass	Transparency of glass	Figure
Chojno-Golejewko	2a	Bead	Ha C	Blue	Very weakly translucent	2.2
Chojno-Golejewko	3a	Bead	Ha C	Blue	Very weakly translucent	2.3
Chojno-Golejewko	4	Bead	Ha C	Blue	Very weakly translucent	2.4
Chojno-Golejewko	5	Bead	Ha C	Blue	Very weakly translucent	2.5
Domasław	6a	Heads of bronze pins	Ha C	Blue	Very weakly translucent	2.6
Domasław	7a	Heads of bronze pins	Ha C	Blue	Very weakly translucent	2.7
Domasław	8a	Bead	Ha C	Blue	Very weakly translucent	2.8
Domasław	8b	Bead	Ha C	Yellow	Opaque	2.8
Domasław	9a	Bead	Ha C	Blue	Very weakly translucent	2.9
Domasław	10a	Bead	Ha C	Blue	Very weakly translucent	2.10
Domasław	11	Bead	Ha C	Blue	Very weakly translucent	2.11
Domasław	12a	Bead	Ha C	Blue	Very weakly translucent	2.12
Domasław	15	Bead	Ha C	Blue	Very weakly translucent	2.15
Domasław	16	Bead	Ha C	Blue	Very weakly translucent	2.16
Domasław	18a	Bead	Ha C	Blue	Very weakly translucent	2.18
Domasław	18b	Bead	Ha C	Yellow	Opaque	2.18
Domasław	19a	Bead	Ha C	Blue	Very weakly translucent	2.19
Domasław	21	Bead	Ha C	Blue	Very weakly translucent	2.21
Gorszewice	24a	Bead	Ha C-Ha C/Ha D	Blue	Very weakly translucent	2.24
Gorszewice	24b	Bead	Ha C-Ha C/Ha D	Yellow	Opaque	2.24
Gorszewice	25a	Bead	Ha C-Ha C/Ha D	Blue	Very weakly translucent	2.25
Gorszewice	25b	Bead	Ha C-Ha C/Ha D	Yellow	Opaque	2.25
Gorszewice	26a	Bead	Ha C-Ha C/Ha D	Blue	Very weakly translucent	2.26
Gorszewice	26b	Bead	Ha C-Ha C/Ha D	Yellow	Opaque	2.26
Kietrz	28	Bead	Ha C	Blue	Very weakly translucent	2.28
Kietrz	29a	Bead	Ha C	Blue	Very weakly translucent	2.29
Kietrz	32	Bead	Ha C	Blue	Very weakly translucent	2.32
Kraków Bieżanów	46a	Bead	Ha C	Blue	Very weakly translucent	2.46
Kraków Bieżanów	46b	Bead	Ha C	Yellow	Opaque	2.46
Orzech	50a	Bead	Ha C?	Blue	Very weakly translucent	2.50
Świbie	64	Bead	Ha C	Blue	Very weakly translucent	2.64
Świbie	66a	Bead	Ha C	Blue	Very weakly translucent	2.66
Świbie	67a	Bead	Ha C	Blue-black	Not transparent	2.67
Świbie	68a	Bead	Ha C	Blue	Very weakly translucent	2.68
Świbie	68b	Bead	Ha C	Yellow	Opaque	2.68
Świbie	69a	Bead	Ha C	Blue	Very weakly translucent	2.69
Świbie	69b	Bead	Ha C	Yellow	Opaque	2.69
Świbie	71a	Bead	Ha C	Blue	Very weakly translucent	2.71
Świbie	72a	Bead	Ha C	Blue-green	Very weakly translucent	2.72
Świbie	73a	Bead	Ha C	Brownish-red	Not transparent	2.73
Świbie	74a	Bead	Ha C	Blue	Very weakly translucent	2.74
Świbie	76a	Bead	Ha C	Blue	Very weakly translucent	2.76
Świbie	76b	Bead	Ha C	Yellow	Opaque	2.76
Świbie	77	Bead	Ha C	Blue	Very weakly translucent	2.77
Świbie	78	Bead	Ha C	Blue	Very weakly translucent	2.78
Świbie	79a	Bead	Ha C	Blue	Very weakly translucent	2.79
Świbie	82a	Bead	Ha C	Blue	Very weakly translucent	2.82
Świbie	83	Bead	Ha C	Blue	Very weakly translucent	2.83

2. Experimental

2.1. Samples

Objects selected for analytical study represented different colors of glassy faience, some decorated with true glass (often the glass had splintered and was preserved as fragments). Altogether 48 different glassy materials from 39 objects were studied, including 39 vitreous phases of glassy faience and nine cases of true glass in the decoration (Table 1).

The ornaments were discovered in southwestern Poland (Fig. 1), in seven cemeteries used by the Lusatian Culture population dated to the Hallstatt C or from Hallstatt C through the turn of Hallstatt C/D. It has recently been suggested that some of these sites can be attributed to a local province of the Hallstatt Culture (Gediga, 2011).

Most of the objects examined represent beads of various sizes (Fig. 2). They are mostly blue in color, either plain or decorated with a decoration of yellow glass forming a straight or wavy line, dots, circles or 'eyes'. Objects decorated in this way can be found in western and southern Poland in contexts dated to the Hallstatt C – beginning of Hallstatt D (Purowski, 2012).

Two heads of bronze pins from the site at Domasław were also studied (Fig. 3). They are blue in color, decorated with straight threads and dots of yellow glass. Objects of this kind are seldom found in central Europe and it is difficult, based on their form alone, to be certain where they could have been produced (Purowski, 2012).

2.2. Analytical techniques

Quantitative analyses of all background glasses (Table 2) and some of the ornamental glasses (Table 3) were carried out using an ELAN 9000 Inductively Coupled Plasma Mass Spectrometer (PerkinElmer SCIEX, Canada) equipped with an LSX-213 laser ablation system (CETAC, USA). The LSX-213 combines a stable, environmentally sealed 213 nm UV laser (Nd–YAG, solid state, Q-switched) with a high sampling efficiency, variable 1–20 Hz pulse repetition rate and maximum energy up to 5 mJ per pulse.

Thirty-six major, minor and trace elements were determined in all the analyzed glass objects. The same analytical procedure and optimal conditions of LA-ICPMS were applied in all measurements as given in Table 4. The samples were placed inside the ablation cell with NIST SRM 610. The standard reference material was measured twice at the beginning and twice at the end of each run to correct the instrumental drift using the algorithm proposed by Longerich et al. (1996). Three replicate single point ablations were carried out on each sample at locations randomly selected on the glass surface. Signal intensities were recorded for the following isotopes: ^{7}Li, ^{11}B, ^{23}Na, ^{26}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{39}K, ^{43}Ca, ^{49}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{61}Ni, ^{65}Cu, ^{66}Zn, ^{75}As, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{95}Mo, ^{109}Ag, ^{118}Sn, ^{121}Sb, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{178}Hf, ^{208}Pb, ^{209}Bi, ^{232}Th and ^{238}U. Transient signals were registered, background corrected and integrated using LAMTRACE software developed by Jackson (2008). The results for all samples were recalculated to the content of the oxides with NIST 610 as the external standard and SiO_2 as the internal standard, applying the sum normalization technique by simultaneous measurements of 36 isotopes and normalizing them to 100 wt % based on their corresponding oxide content.

The accuracy of the measurements was established by comparison of the results for two archeological reference glasses: Corning B and Corning D to the values recommended in the literature (Brill, 1972, 1999; Vicenzi et al., 2002; Dussubieux et al., 2009; Wagner et al., 2012). They were examined as for the unknown

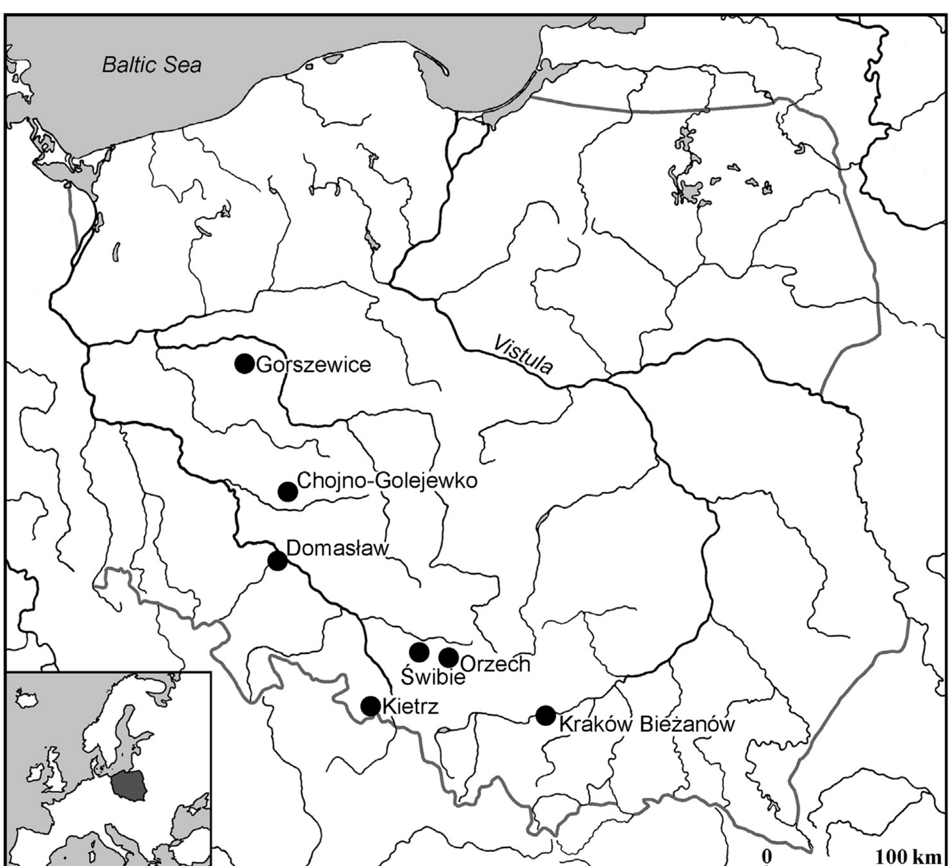

Fig. 1. Localities of archaeological sites in southwestern Poland that have yielded glassy faience finds analyzed in this study.

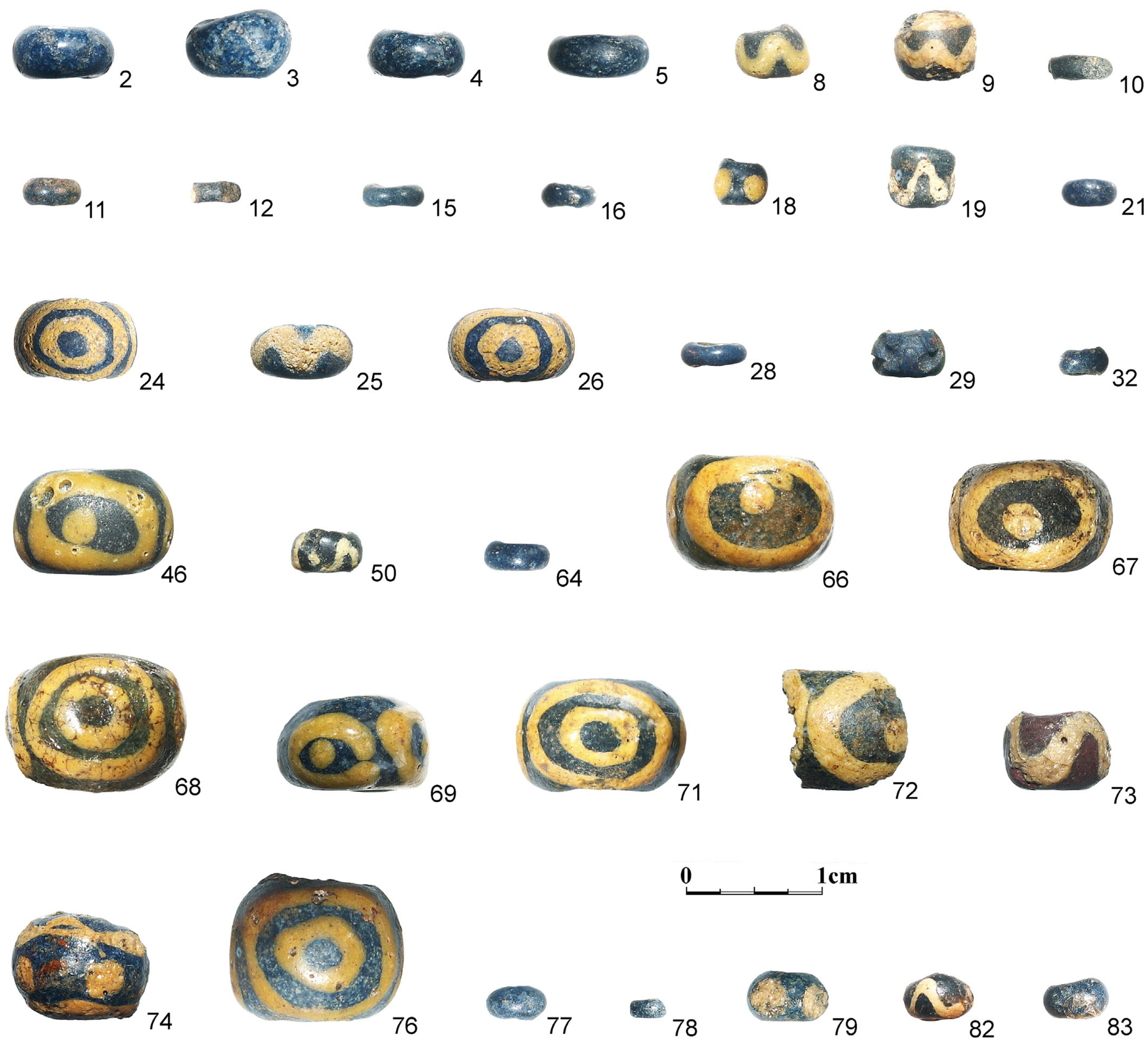

Fig. 2. Beads subjected to physico-chemical analysis (numbers next to objects refer to sample number in Tables 1–3).

samples. The contents of 27 oxides in Corning B and D are given in Table 5 with respect to the values indicated by Wagner et al. (2012), Dussubieux et al. (2009) and Brill (1972, 1999).

Samples from which polished sections could be made were also examined with a Cameca SX100 electron microprobe furnished with WDS and EDS spectrometers, allowing simultaneous electron microscopy and precise chemical analysis of selected microfragments. The best results were obtained by examining backscattered electron images (BSE) that reflect local changes of chemical composition. The BSE image contrast is dependent on the mean atomic number of the sample at the point where the electron beam interacts with the analyzed material. The method is particularly informative for materials of variable composition, such as glassy faience, because it easily differentiates between true glass and various solid inclusions, and determines the chemical composition of the glass and each inclusion separately. The present study has been based primarily on electron microscopy observations, supplemented by data on the chemical composition of the inclusions to the extent that this has improved the interpretation of the ICP results. Detailed EPMA results for the different inclusions – pigments, impurities from the raw material and phases newly formed in the technological process – will be the object of separate study.

3. Results

3.1. Glassy faience and true glass: microstructure

Glassy faience from the examined collection is composed of glass and numerous relict grains of raw material, mainly quartz (Fig. 4). Single, not completely melted, grains of other components from the raw material, e.g., feldspar and accessory minerals present in sand, such as zircon, rutile and magnetite, were also identified. Phases formed during the cooling of the material or their

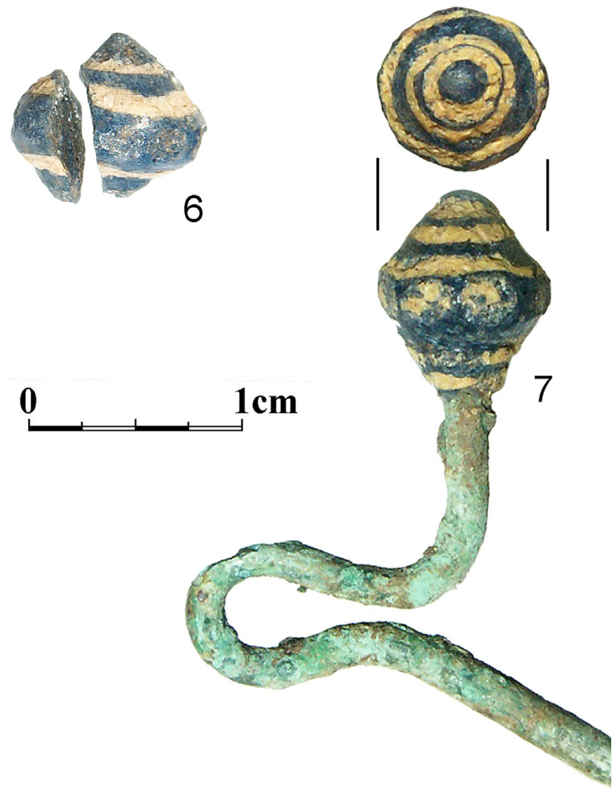

Fig. 3. Pin heads subjected to physico-chemical analysis (numbers next to objects refer to sample number in Tables 1 and 2).

devitrification were also identified in some samples, e.g. wollastonite. As relict quartz grains can be of different shapes and sizes, even if partially melted, they can retain sufficient morphological characteristics that allow determination of the sources of the quartz raw material, e.g. well sorted, rounded quartz grains indicate natural sandy raw materials as the source, while sharp-edged quartz grains of different size come rather from crushed quartz raw material. BSE images also show numerous gas bubbles of varied size (mostly small, but some exceed 100 μm in diameter) in the glassy faience.

Inclusions merit particular attention. They can be perfectly round or irregular in shape, but usually rounded, made up of Fe, Co, Ni, Cu, Zn, Ag, Pb, Sn, Sb, S and As, which are frequent as ores in nature. Their presence in the raw material may be due to pulverized ore or the partial products of the melting of metal introduced for color effect. The irregularly shaped inclusions most often represent sulfides with chalcocite composition (Cu_2S), a common copper ore, or iron oxides from the sand. The round inclusions, which are multiphase as a rule, are more varied in composition. They were most probably the product of melting of a mixture of polymetallic ores and quartz raw material in the glass-melting process or they came from the polymetallic ores added to the glass melt. During the cooling process the alloys crystallized, forming characteristic symplectic intergrowths, depending on the composition in a given droplet. Examples of inclusions with composition: (i) Pb, Cu; (ii) Pb, Cu, S; (iii) Pb, Cu, Ni, S; (iv) Ag, Ni, Pb, Sb, Cu, As, have been shown in Fig. 5a–e and Table 6. These inclusions are most often of small size, generally up to 60 μm in diameter, but reaching 200 μm in length in singular cases. Inclusions of spinel are composed mainly of Fe, Co and Ni, and in smaller quantities also of Al, Mg, Sn and Cu (Fig. 5f–h; Table 7). A zone of diffusion expressed by higher concentrations of metals forming spinel can be observed in them.

Colorant inclusions are extremely numerous in the glass of the decoration (Fig. 4d). They occur as isolated isometric grains usually no more than 1 μm in size (most often < 0.5 μm), fairly evenly dispersed in the glass or concentrated in aggregates a few dozen microns in size. Three inclusions of this type in sample 18b were analyzed by EPMA and were found to be composed mainly of PbO (approx. 56%–59%) and Sb_2O_5 (approx. 30%–34%), with smaller amounts of FeO (about 5%) (Table 8). Gas bubbles and single unreacted quartz grains are found less often in the glass of the decoration. Despite the presence of these inclusions, the material discussed should be treated as true glass.

3.2. Chemical composition of the glass

The 39 glasses making up the glassy faience, the material examined in this study, differ in the contents of some of the major and trace elements. Comparing the MgO to K_2O ratio, one can distinguish two groups: (i) low magnesium and medium potassium (LMMK) – 25; (ii); low magnesium and low potassium (designated with the symbol LMG_{GF}, that is, low magnesium glass of glassy faience, to distinguish it from the LMG true glass) – 13. The LMMK glass has 0.5–1.0% MgO and most often >1.5% K_2O, whereas LMG_{GF} show a prevalent concentration of <0.5% MgO and most often <1.5% K_2O (Fig. 6). One glass cannot be classified according to the above division: sample no. 78 has a much higher concentration of MgO (1.68%) compared to that in the other glassy faience discussed in the present article.

Nine true glasses representing the decoration can be assigned to LMG glass with low levels of MgO (<0.6%) and K_2O (<0.5%) (Fig. 7).

3.2.1. Glassy faience – LMMK and LMG_{GF} glass

The LMMK glass in the collection features substantial alkali contents: 11.50%–19.58% Na_2O (average 15%) and 1.26%–6.25% K_2O (average 2.7%). Glass sample no. 15 is distinctive as it has a much higher concentration of K_2O. A fairly high concentration was also noted for sample no. 73a, but neither glass had a high amount of Na_2O. Alkali oxide content in LMG_{GF} glass is lower: 7.26%–13.93% Na_2O (average 11%) and 0.35%–1.55% K_2O (average 0.9%).

The low MgO (0.54%–1.00%) and CaO (1.61%–3.58%) in the LMMK glass is noteworthy. Only the sample from Świbie (no. 73a) had 6.54% CaO. Low levels of the two components were also observed in LMG_{GF} glass: 0.19%–0.53% MgO and 1.78%–3.83% CaO; slightly more MgO (0.72%) was found only in sample no. 46a.

LMMK glass has a high concentration of aluminum and iron oxides: 2.62%–8.13% Al_2O_3 (average 5.6%) and 2.12%–7.43% Fe_2O_3 (average 4.2%). Lower values, especially of aluminum compounds, were noted in LMG_{GF} glass: 0.57%–2.48% Al_2O_3 (average 1.1%), 1.24%–7.01% Fe_2O_3 (average 3.3%).

One of the main characteristics of LMMK glass is the relatively high content of trace elements, such as boron (0.72%–1.64% B_2O_3), titanium (0.20%–0.48% TiO_2) and barium (0.03%–0.06% BaO). LMG_{GF} glass in the collection did not have more than 0.2% of the first two (Fig. 8), whereas BaO ≤ 0.02%; only sample no. 68a had a higher concentration of B_2O_3 (0.76%).

In discussing the components that could have had an effect on the color and transparency of the tested materials, one should emphasize that most glasses forming glassy faience were revealed to have higher concentrations of the same compounds regardless of the color. Blue LMMK and LMG_{GF} glass (36 examples), blue–black (one example) or blue–green (one example) contained cobalt (0.11%–0.82% CoO), iron (1.24%–7.43% Fe_2O_3), copper (0.21%–2.06% CuO) and manganese (0.02%–0.37% MnO). The high concentrations of lead and antimony are notable, and are higher in LMG_{GF} glass than in LMMK glass (Fig. 9). Similar levels of all the listed

Table 2
Chemical composition of glass forming glassy faience (oxides wt%) and relative standard deviation values (RSD, %) obtained with LA-ICPMS (abbreviations: <LOD = below the limit of detection of the method).

Site and sample no.	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3	MnO	Sb_2O_5	PbO	CoO	CuO	BaO	TiO_2	SnO_2	NiO	ZnO	As_2O_5	P_2O_5	B_2O_3
LOD	0.1030	0.0001	0.0002	0.0092	0.0006	0.0002	0.0015	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0005	0.0001	0.0023	0.0003	0.0002	0.0016	0.0007
Low magnesium and medium potassium glass (LMMK)																				
Chojno-Golejewko 2a	64.76	13.22	2.22	2.49	0.69	4.53	2.22	0.20	0.38	4.84	0.27	1.51	0.04	0.29	0.04	0.10	0.04	0.07	0.21	0.90
RSD	0.4	1.2	0.7	3.5	1.7	0.4	2.4	0.8	4.2	11.4	1.5	17.9	1.3	2.1	4.3	3.7	3.5	22.3	46.7	4.5
Chojno-Golejewko 3a	66.23	11.50	2.45	2.29	0.58	4.57	2.26	0.18	0.38	5.63	0.31	1.48	0.05	0.27	0.05	0.10	0.05	0.08	0.13	0.87
RSD	1.7	6.5	3.1	12.4	8.0	3.7	2.5	4.2	5.1	6.0	5.6	8.9	6.6	7.5	9.1	2.5	5.9	12.0	9.7	3.9
Chojno-Golejewko 4	64.22	13.66	2.36	2.49	0.78	5.08	3.71	0.25	0.33	2.88	0.42	1.11	0.04	0.38	0.15	0.16	0.05	0.10	0.13	1.25
RSD	5.6	10.1	9.7	11.3	9.2	13.0	10.7	7.0	10.6	6.8	5.0	4.5	10.1	11.0	18.8	6.6	3.5	8.8	14.7	11.6
Chojno-Golejewko 5	68.90	12.45	1.54	2.23	0.61	3.10	2.12	0.18	0.36	5.82	0.29	0.42	0.03	0.20	0.05	0.09	0.03	0.03	<0.19	0.77
RSD	1.3	4.5	4.5	4.3	12.9	2.1	14.1	7.2	2.1	3.0	12.6	11.1	6.8	7.0	49.7	18.5	9.0	4.4		2.0
Domasław 6a	65.98	15.47	2.62	1.66	0.63	6.13	3.79	0.37	0.10	0.47	0.22	<0.60	0.04	0.35	0.004	0.08	0.02	0.03	0.10	1.47
RSD	1.5	2.1	3.1	2.7	1.4	2.3	6.9	0.9	22.1	13.4	5.3		3.0	2.7	41.0	19.9	4.6	41.2	6.6	2.6
Domasław 8a	63.84	15.89	2.27	1.96	0.71	6.24	5.11	0.22	0.13	<0.41	0.24	0.74	0.04	0.35	0.01	0.10	0.02	0.03	0.13	1.35
RSD	0.7	1.3	0.9	1.9	1.9	3.1	4.8	1.2	19.6		3.9	36.9	4.8	2.5	3.9	5.5	2.1	7.5	3.0	3.2
Domasław 9a	66.66	14.56	2.77	1.92	0.70	6.00	3.35	0.17	0.15	0.93	0.19	0.55	0.03	0.30	0.25	0.08	0.01	0.04	0.09	0.78
RSD	0.9	1.9	5.5	9.8	3.5	5.4	12.1	3.9	13.0	4.1	6.8	14.9	9.8	3.9	12.4	19.8	20.6	20.1	3.6	6.2
Domasław 10a	64.85	12.82	3.54	1.75	0.61	5.81	5.21	0.18	0.34	0.44	0.54	0.89	0.03	0.32	0.06	0.27	0.02	0.32	0.10	1.16
RSD	2.7	3.6	7.9	2.0	2.5	4.8	6.7	3.1	7.9	0.9	1.2	41.2	3.4	4.3	2.7	44.9	44.2	47.4	3.9	3.3
Domasław 11	62.19	14.30	2.37	1.62	0.59	5.77	5.51	0.33	0.22	3.75	0.36	0.43	0.04	0.31	0.04	0.15	0.02	0.18	0.09	1.35
RSD	2.9	2.5	4.3	6.4	2.7	4.0	14.8	4.5	6.9	3.2	10.9	6.5	4.1	2.7	6.4	4.2	5.2	4.3	1.3	0.9
Domasław 15	60.76	13.73	6.25	3.58	0.86	7.06	4.46	0.24	0.11	0.15	<0.24	0.35	0.05	0.36	0.02	0.20	0.02	0.10	0.17	1.10
RSD	3.5	1.7	10.3	8.3	2.9	8.7	51.9	6.1	9.7	3.7		2.5	1.6	2.8	25.7	73.6	17.2	22.5	7.4	3.1
Domasław 16	62.82	15.66	3.86	2.45	0.69	6.23	3.45	0.26	0.26	0.58	0.28	0.84	0.04	0.38	0.09	0.20	0.02	0.05	0.15	1.22
RSD	0.9	2.6	2.1	2.7	2.1	2.0	1.6	1.9	7.3	5.8	3.4	13.0	7.1	2.3	2.2	9.0	1.7	14.9	14.2	2.1
Domasław 18a	61.20	17.86	2.29	2.10	0.69	6.55	4.43	0.28	0.26	0.55	0.39	0.55	0.04	0.37	0.11	0.38	0.03	0.04	0.18	1.27
RSD	0.6	1.2	4.2	8.8	3.9	4.9	6.9	3.6	3.1	4.8	16.3	3.7	4.3	4.4	14.9	35.5	9.7	7.8	25.0	3.9
Domasław 19a	63.82	15.08	2.40	1.61	0.58	5.92	3.76	0.34	0.19	2.87	0.21	0.48	0.04	0.36	0.03	0.10	0.01	0.14	0.19	1.44
RSD	1.1	3.1	4.9	0.6	3.3	4.4	4.3	1.5	12.5	35.9	6.5	42.5	1.8	4.1	17.2	39.0	4.5	2.0	46.3	1.9
Domasław 21	65.43	16.30	2.70	1.78	0.59	5.69	3.17	0.31	0.15	0.70	0.41	0.54	0.03	0.34	0.07	0.18	0.03	0.02	0.12	1.01
RSD	0.8	1.2	3.2	4.4	1.3	3.3	1.5	3.0	10.3	6.7	0.9	7.7	3.9	2.9	6.8	3.6	3.1	11.8	22.5	3.0
Gorszewice 25a	63.51	13.58	2.82	2.38	0.67	4.78	2.71	0.23	<0.60	6.54	0.24	<2.03	0.04	0.34	0.03	<0.19	0.06	<0.30	0.22	1.07
RSD	1.9	6.9	13.3	9.3	8.1	8.6	14.5	10.9		28.6	14.5		16.3	6.9	6.7		49.1		42.8	13.0
Kietrz 28	71.14	11.54	1.65	1.71	0.55	5.12	6.68	0.28	0.11	0.95	0.32	0.55	0.04	0.30	0.03	0.16	0.03	0.04	0.14	1.30
RSD	2.8	8.5	8.5	11.4	7.4	7.7	13.6	7.9	10.5	9.7	19.7	11.6	8.9	6.8	15.5	15.7	8.8	30.7	11.7	8.1
Kietrz 29a	68.23	12.43	1.92	1.85	0.64	5.97	7.43	0.34	0.11	1.07	0.32	0.45	0.04	0.34	0.04	0.09	0.02	0.03	0.10	1.56
RSD	1.3	7.5	3.5	5.6	2.5	2.2	3.7	2.7	3.2	16.9	1.8	12.5	1.4	3.8	22.3	6.8	8.5	6.4	3.7	6.4
Kietrz 32	63.61	16.56	2.02	2.97	0.54	3.56	4.37	0.23	0.39	4.70	0.19	0.63	0.03	0.25	0.15	0.14	0.02	0.02	0.12	0.82
RSD	4.3	15.2	2.5	6.3	5.2	6.7	7.3	6.4	7.2	8.5	6.2	14.9	9.1	7.1	8.9	10.5	3.8	16.5	14.8	9.0
Orzech 50a	64.25	17.93	1.93	1.69	1.00	5.32	4.56	0.28	0.64	0.14	0.16	1.02	0.04	0.39	0.002	0.21	0.01	0.25	0.11	1.32
RSD	0.6	0.7	2.9	6.0	3.5	2.7	0.2	4.0	4.3	2.5	0.2	22.9	3.7	3.0	5.5	21.4	6.7	19.7	2.9	2.0
Świbie 64	56.27	19.58	2.52	2.99	0.98	8.13	3.68	0.28	0.36	1.09	0.63	0.59	0.05	0.48	0.01	0.29	0.07	0.07	0.12	1.47
RSD	0.4	1.5	1.0	2.6	1.0	3.5	5.6	0.6	10.2	1.6	5.7	22.6	1.6	2.1	6.2	4.2	6.4	28.1	3.7	2.8
Świbie 73a	60.03	11.74	4.91	6.54	0.71	3.68	7.38	0.14	0.50	1.61	0.25	1.34	0.04	0.29	0.06	0.14	0.02	0.09	1.84	0.79
RSD	0.9	4.1	1.6	3.3	2.5	8.6	3.6	1.1	1.9	3.4	1.2	7.3	5.8	4.4	1.5	4.0	13.3	6.1	2.0	1.4
Świbie 76a	62.48	15.53	1.26	2.85	0.61	2.62	4.81	0.15	0.69	5.66	0.50	0.67	0.04	0.25	0.17	0.52	0.07	0.03	0.09	0.72
RSD	3.3	13.1	6.8	17.6	16.2	7.3	21.5	5.1	5.9	6.6	12.6	12.3	9.5	6.7	3.4	12.4	7.4	25.3	1.3	6.8
Świbie 79a	61.56	17.14	3.02	2.06	0.75	7.74	3.17	0.35	0.16	0.58	0.29	0.29	0.06	0.41	0.01	0.12	0.02	0.02	0.11	1.64
RSD	0.5	0.6	1.4	3.0	1.7	0.8	4.4	3.3	4.7	4.5	2.7	3.0	1.2	2.7	4.8	4.1	4.2	9.4	4.0	3.8
Świbie 82a	62.76	17.13	2.52	2.17	0.79	6.85	3.78	0.28	0.06	0.28	0.29	0.38	0.04	0.38	0.02	0.09	0.02	0.01	0.11	1.51
RSD	1.7	2.4	5.5	2.4	2.5	3.2	2.4	1.9	3.5	5.1	5.7	37.0	2.8	2.7	1.4	5.4	4.0	2.0	1.5	1.8
Świbie 83	57.66	18.40	3.09	2.78	0.78	7.28	2.67	0.29	0.26	3.45	0.22	0.39	0.06	0.41	0.02	0.11	0.02	0.02	0.11	1.42
RSD	0.3	3.0	1.6	2.9	1.8	3.2	1.8	0.9	5.3	0.5	3.9	4.7	1.7	1.9	1.6	4.4	5.8	14.8	1.9	5.4

(*continued on next page*)

Table 2 (*continued*)

Site and sample no.	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3	MnO	Sb_2O_5	PbO	CoO	CuO	BaO	TiO_2	SnO_2	NiO	ZnO	As_2O_5	P_2O_5	B_2O_3
Low magnesium glass of glassy faience (LMG_{GF})																				
Domasław 7a	63.99	13.28	1.14	2.60	0.28	1.59	5.89	0.06	0.94	7.48	0.33	0.64	0.02	0.20	0.03	0.15	0.03	0.02	0.07	0.20
RSD	0.5	2.8	1.0	2.0	1.2	3.1	1.6	1.2	4.1	5.4	2.7	10.4	1.7	0.7	2.7	6.1	0.8	7.5	7.6	7.0
Domasław 12a	67.60	11.67	1.55	1.88	0.19	0.85	1.24	0.03	1.55	9.72	0.82	1.03	0.01	0.14	0.03	1.02	0.01	0.69	0.05	0.15
RSD	3.5	7.3	9.9	4.5	4.3	7.8	5.1	5.0	4.5	4.3	9.1	21.8	3.7	6.0	3.6	5.6	7.9	2.7	9.0	4.1
Gorszewice 24a	63.81	11.50	0.89	2.02	0.36	1.00	2.65	0.02	0.92	13.70	0.54	0.81	0.01	0.13	0.01	0.25	0.04	0.02	0.12	0.04
RSD	2.9	9.3	14.4	1.9	9.1	0.7	9.0	13.7	5.5	4.4	3.3	39.9	30.6	3.4	17.1	16.8	8.6	5.8	38.7	9.5
Gorszewice 26a	60.55	12.23	1.07	2.17	0.35	1.15	2.72	0.02	0.91	15.75	0.56	1.05	0.01	0.14	0.01	0.27	0.05	0.03	0.32	0.05
RSD	2.0	1.7	2.3	9.4	5.5	11.0	14.8	20.3	7.6	5.3	1.8	48.9	10.5	4.1	40.3	4.1	36.5	15.8	27.2	16.7
Kraków Bieżanów 46a	64.98	7.26	0.65	2.71	0.72	1.03	3.10	0.03	1.59	15.65	0.17	0.75	0.01	0.07	0.02	0.32	0.02	0.26	0.06	0.04
RSD	2.6	8.4	17.5	9.6	9.0	8.1	9.2	13.2	1.2	3.1	8.1	15.6	3.8	17.1	3.4	11.4	4.2	0.4	20.5	6.4
Świbie 66a	67.80	13.93	0.63	3.83	0.50	0.72	3.47	0.32	1.09	6.81	0.24	1.02	0.01	0.08	0.05	0.29	0.03	0.15	0.17	0.05
RSD	3.4	3.9	3.6	3.1	5.6	9.7	0.3	2.6	6.6	7.4	8.1	2.0	8.5	4.8	34.8	5.0	7.5	0.7	21.0	3.7
Świbie 67a	78.55	7.93	0.35	1.78	0.29	0.61	2.18	0.15	1.24	3.83	0.25	0.46	0.004	0.04	0.04	0.37	0.02	0.18	0.63	0.07
RSD	1.1	3.4	16.3	3.4	7.6	0.8	4.4	4.0	7.7	1.3	9.4	5.5	12.3	10.5	12.0	7.5	10.5	7.4	16.5	4.8
Świbie 68a	62.11	11.41	0.94	2.17	0.53	2.48	1.45	0.11	0.65	6.85	0.11	2.06	0.02	0.17	1.15	0.13	0.05	0.09	0.15	0.76
RSD	4.0	1.6	6.8	8.7	0.3	5.9	8.3	8.0	7.3	10.5	10.1	8.0	11.3	11.7	44.3	9.1	19.7	7.1	8.7	3.8
Świbie 69a	67.62	10.52	0.89	3.01	0.50	0.91	2.98	0.05	1.67	9.48	0.39	0.42	0.01	0.10	0.03	0.37	0.03	0.30	0.12	0.09
RSD	5.4	9.4	19.9	10.0	9.3	0.9	0.0	4.9	5.6	2.9	2.8	9.1	22.6	5.1	48.3	5.9	6.7	7.1	5.4	9.4
Świbie 71a	58.42	8.56	0.75	2.23	0.30	2.09	7.01	0.02	1.60	15.66	0.31	0.21	0.01	0.10	0.22	0.43	0.02	0.58	2.12	0.05
RSD	0.5	11.1	6.4	3.5	6.1	7.3	3.4	4.7	8.4	5.7	9.0	4.1	6.8	2.5	1.2	6.6	11.0	6.0	17.7	6.6
Świbie 72a	61.78	12.75	0.67	3.31	0.44	0.57	1.42	0.29	1.18	15.12	0.29	0.86	0.01	0.07	0.06	0.50	0.02	0.12	0.14	0.04
RSD	1.9	5.1	20.8	3.8	5.8	14.8	10.7	5.3	11.4	4.2	22.4	35.1	12.2	9.1	46.6	27.6	25.0	15.1	50.0	9.8
Świbie 74a	66.26	13.52	0.86	2.97	0.43	1.14	5.43	0.07	0.74	7.17	0.63	0.50	0.01	0.14	0.05	0.21	0.04	0.02	0.07	0.14
RSD	2.1	10.6	9.1	13.0	2.0	1.9	28.5	14.3	15.7	12.7	57.5	1.6	7.4	14.2	17.7	17.6	47.3	8.6	18.7	15.7
Świbie 77	63.09	10.97	1.43	3.59	0.24	0.58	2.82	0.04	0.76	14.65	0.40	0.35	0.01	0.09	0.07	0.14	0.04	0.01	0.07	0.03
RSD	1.9	22.5	8.4	4.8	5.6	14.5	5.9	3.9	5.5	5.3	5.9	25.3	5.0	8.1	10.2	8.2	11.4	3.0	16.1	21.7
Other																				
Świbie 78	64.73	17.81	1.68	4.73	1.68	0.54	2.55	0.05	0.27	2.77	0.26	1.78	0.01	0.06	0.06	0.23	0.03	0.10	0.19	0.06
RSD	1.0	3.9	4.3	1.7	1.2	12.3	8.3	1.3	2.9	3.7	0.7	11.9	4.8	7.3	7.4	2.9	3.3	4.5	16.9	0.5

Site and sample no.	Cs_2O	V_2O_5	Rb_2O	SrO	Y_2O_3	ZrO_2	MoO_2	Ag_2O	La_2O_3	Ce_2O_3	HfO_2	Bi_2O_3	ThO_2	UO_2	Li_2O	Cr_2O_3
LOD	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0004
Low magnesium and medium potassium glass (LMMK)																
Chojno-Golejewko 2a	0.0001	0.0098	0.0049	0.0156	0.002	0.0156	<LOD	<0.014	0.002	0.0029	<LOD	<LOD	0.001	<LOD	0.0127	0.0029
RSD	27.5	5.7	8.2	3.5	3.7	0.3			3.1	2.7			1.1		4.6	9.6
Chojno-Golejewko 3a	0.0001	0.0039	0.0049	0.0158	0.002	0.0158	<LOD	0.0089	0.002	0.003	<LOD	<LOD	0.001	<LOD	0.0109	0.003
RSD	5.9	4.1	1.0	8.7	9.0	7.2		4.8	4.4	12.7			2.6		8.3	2.3
Chojno-Golejewko 4	0.0001	0.006	0.006	0.0199	0.002	0.0199	0.001	0.009	0.002	0.004	0.001	<LOD	0.001	<LOD	0.0183	0.004
RSD	10.8	9.5	10.4	9.4	15.6	14.8	8.5	13.6	3.7	8.9	15.3		12.7		13.8	12.8
Chojno-Golejewko 5	0.0001	0.0039	0.0029	0.0137	0.001	0.0107	<LOD	0.001	0.001	0.002	<LOD	<LOD	<LOD	<LOD	0.0089	0.002
RSD	26.9	8.5	1.6	3.8	2.4	1.9		44.6	3.5	6.7					2.1	21.3
Domasław 6a	<LOD	0.005	0.006	0.017	0.002	0.018	<LOD	<0.008	0.002	0.003	<LOD	0.001	0.001	<LOD	0.0208	0.004
RSD		3.3	5.5	3.6	4.8	2.6			3.7	2.3		22.4	9.2		4.4	2.8
Domasław 8a	<LOD	0.006	0.005	0.015	0.002	0.016	0.001	<0.006	0.002	0.003	<LOD	<LOD	0.001	<LOD	0.0145	0.004
RSD		3.8	1.3	2.7	6.5	2.4	2.8		3.1	1.6			7.0		2.4	13.2
Domasław 9a	<LOD	0.0056	0.006	0.0139	0.002	0.0139	<LOD	0.001	0.002	0.003	<LOD	<LOD	0.001	<LOD	0.0087	0.004
RSD		3.9	3.1	11.3	5.7	3.8		47.8	4.6	5.6			1.1		2.4	15.1
Domasław 10a	<LOD	0.005	0.007	0.0139	0.002	0.0159	0.001	<0.010	0.002	0.003	<LOD	0.002	0.001	<LOD	0.0159	0.004
RSD		3.1	4.1	5.0	2.0	4.9	8.4		1.9	2.7		34.5	4.1		6.1	3.4
Domasław 11	<LOD	0.0049	0.0058	0.0156	0.0019	0.0156	0.001	0.0019	0.0019	0.0029	<LOD	0.001	0.001	<LOD	0.0188	0.0029
RSD		5.6	5.5	2.9	4.0	3.4	18.6	36.3	5.3	5.5		20.2	5.7		4.2	3.6
Domasław 15	<LOD	0.006	0.011	0.019	0.002	0.019	<LOD	0.001	0.002	0.004	0.001	<LOD	0.001	<LOD	0.012	0.004
RSD		2.3	21.2	1.8	1.8	2.7		21.5	1.8	1.2	3.3		1.7		1.1	3.8
Domasław 16	<LOD	0.006	0.006	0.0169	0.002	0.0179	0.001	0.005	0.002	0.004	<LOD	0.003	0.001	<LOD	0.0159	0.004
RSD		4.1	6.2	1.3	1.6	2.2	9.3	52.3	4.9	1.0		37.4	2.3		1.0	9.3

Domasław 18a	<LOD	0.006	0.005	0.016	0.002	0.018	0.001	0.002	0.002	0.003	<LOD	0.001	0.001	0.001	0.0149	0.004
RSD		4.9	4.1	2.8	3.0	3.7	2.3	9.6	6.6	4.5		8.8	6.1	1.9	4.2	4.3
Domasław 19a	<LOD	0.006	0.006	0.0169	0.002	0.0169	<LOD	0.003	0.002	0.003	<LOD	0.001	0.001	<LOD	0.0201	0.005
RSD		7.6	3.3	4.2	5.4	3.2		44.3	13.8	10.8		14.1	3.6		1.8	15.6
Domasław 21	<LOD	0.006	0.006	0.015	0.002	0.0169	<LOD	0.001	0.001	0.003	<LOD	<LOD	<LOD	<LOD	0.0159	0.005
RSD		4.1	6.2	2.5	3.8	3.0		26.7	1.2	1.3					4.6	1.6
Gorszewice 25a	<LOD	0.0051	0.0072	0.0175	0.0021	0.0164	<LOD	<0.032	0.0021	0.0031	<LOD	<0.001	0.001	<LOD	0.0203	0.0041
RSD		11.9	10.5	16.0	12.5	20.9			9.0	8.5			11.6		7.0	17.3
Kietrz 28	0.0001	0.0044	0.005	0.0159	0.0017	0.0146	0.0004	0.0023	0.0014	0.0027	0.0004	0.0011	0.0004	0.0002	0.0115	0.0036
RSD	9.7	6.5	8.0	9.9	9.0	9.6	9.3	58.1	8.0	8.5	10.8	12.5	8.0	9.3	7.8	10.7
Kietrz 29a	0.0002	0.0053	0.006	0.017	0.0019	0.0172	0.0004	0.0014	0.0017	0.0034	0.0004	0.0007	0.0005	0.0002	0.011	0.0043
RSD	17.9	8.1	5.9	4.6	2.5	4.1	6.8	25.9	7.2	12.5	3.2	10.6	5.0	4.9	11.0	7.8
Kietrz 32	0.0001	0.0041	0.0045	0.0167	0.0014	0.0151	0.0003	0.0016	0.0013	0.0025	0.0003	0.0004	0.0003	0.0003	0.0049	0.0037
RSD	20.9	4.9	6.7	7.9	5.3	16.2	8.4	30.1	5.9	5.9	9.9	87.9	11.1	5.6	0.6	8.4
Orzech 50a	0.0002	0.0069	0.0061	0.0152	0.002	0.0181	0.0002	0.0162	0.0018	0.0035	0.0004	0.0066	0.0006	0.0004	0.0144	0.0062
RSD	5.9	0.3	4.7	2.6	5.5	4.3	4.7	56.3	4.8	0.9	6.8	12.8	1.2	3.1	3.3	6.4
Świbie 64	<LOD	0.008	0.006	0.0199	0.003	0.0249	0.001	<0.007	0.002	0.004	0.001	0.001	0.001	<LOD	0.0135	0.006
RSD		4.6	1.6	1.0	5.6	3.3	3.7		1.5	2.5	6.8	26.3	6.2		3.0	4.6
Świbie 73a	0.0001	0.0049	0.0071	0.0187	0.0016	0.016	0.0003	0.0069	0.0016	0.0032	0.0004	0.0027	0.0005	0.0003	0.0104	0.0033
RSD	4.9	1.8	1.2	4.8	6.8	7.3	8.1	57.7	8.6	7.2	7.1	6.3	6.3	2.9	1.8	6.2
Świbie 76a	<LOD	0.004	0.0039	0.016	0.0011	0.0142	0.0003	0.0087	0.001	0.0019	0.0003	0.0002	0.0003	0.0004	0.0124	0.0029
RSD		9.3	5.8	21.0	7.0	7.1	37.5	100.6	8.6	3.8	12.2	4.7	5.3	5.9	9.9	11.6
Świbie 79a	<LOD	0.006	0.007	0.0219	0.003	0.0219	<LOD	0.001	0.002	0.004	0.001	0.001	0.001	0.001	0.0192	0.005
RSD		5.4	3.3	0.7	5.0	2.8		4.9	3.9	1.7	3.7	8.4	3.6	6.5	3.0	4.3
Świbie 82a	<LOD	0.006	0.006	0.0179	0.002	0.0189	0.001	0.002	0.002	0.004	0.001	<LOD	0.001	<LOD	0.0178	0.005
RSD		2.7	3.3	2.2	4.9	2.4	4.5	63.0	1.7	1.3	2.8		1.9		3.3	5.7
Świbie 83	<LOD	0.0068	0.0068	0.0196	0.0029	0.0215	<LOD	0.001	0.002	0.0039	0.001	<LOD	0.001	<LOD	0.0161	0.0049
		2.2	2.7	2.9	3.5	2.1		7.8	1.6	3.3	5.6		2.0		2.3	4.1
Low magnesium glass of glassy faience (LMG$_{GF}$)																
Domasław 7a	0.0001	0.0023	0.003	0.0119	0.0012	0.0153	0.0005	0.0016	0.0009	0.0015	0.0003	0.0002	0.0002	0.0002	0.0014	0.0018
RSD	8.2	2.9	5.8	0.6	2.7	2.2	0.5	5.1	1.3	3.7	7.4	10.1	4.8	8.2	2.9	7.3
Domasław 12a	<LOD	0.002	0.002	0.008	0.001	0.015	<LOD	0.003	0.001	0.001	<LOD	0.002	<LOD	<LOD	0.0019	0.002
RSD		12.7	10.9	2.8	4.1	3.3		23.0	5.4	4.1		1.5			3.9	14.1
Gorszewice 24a	<LOD	0.002	0.004	0.009	0.001	0.014	<LOD	0.002	0.001	0.002	<LOD	<0.0003	<LOD	0.001	0.0014	0.003
RSD		15.9	6.7	7.1	5.8	6.7		25.0	3.2	9.1				10.5	40.9	30.8
Gorszewice 26a	<LOD	0.002	0.004	0.0089	0.001	0.0158	<LOD	0.002	0.001	0.002	<LOD	<LOD	<LOD	0.001	0.0014	0.003
RSD		13.7	6.6	5.3	8.9	5.1		21.7	29.6	9.1				4.5	46.6	46.3
Kraków Bieżanów 46a	<LOD	0.0019	0.0009	0.0098	0.0003	0.0023	<LOD	0.0356	0.0004	0.0008	0.0001	0.0003	0.0001	0.0003	<0.0002	0.0024
RSD		14.3	6.9	5.2	2.6	3.3		64.2	11.2	11.9	64.7	1.3	6.9	2.6		13.3
Świbie 66a	<LOD	0.0023	0.0033	0.0144	0.0004	0.0096	0.0002	0.0027	0.0004	0.0007	0.0002	0.0007	0.0001	0.0004	0.0004	0.0016
RSD		4.7	6.4	3.7	9.7	7.6	7.8	94.0	3.0	18.0	1.9	12.1	9.9	5.0	6.4	16.7
Świbie 67a	<LOD	0.0011	0.002	0.0068	0.0003	0.0054	<LOD	0.0026	0.0003	0.0006	<LOD	0.0003	<LOD	0.0002	<LOD	<LOD
RSD		42.4	26.6	18.8	2.5	11.7		4.3	2.4	17.3		6.7		6.5		
Świbie 68a	0.0001	0.0031	0.0021	0.0105	0.001	0.0095	0.0002	0.0068	0.0009	0.0017	0.0002	0.0006	0.0003	0.0003	0.0041	0.0021
RSD	29.3	11.0	8.1	9.2	14.0	10.1	10.9	6.3	5.5	5.1	19.1	7.4	10.9	11.2	0.4	17.3
Świbie 69a	<LOD	0.0017	0.0013	0.0113	0.0005	0.0088	0.0001	0.0011	0.0005	0.0008	0.0002	0.0002	0.0001	0.0004	0.0005	0.0018
RSD		13.0	17.1	4.9	7.6	8.7	46.4	2.7	9.1	5.1	8.7	2.6	18.8	4.7	31.2	6.8
Świbie 71a	<LOD	0.0037	0.0041	0.0081	0.0008	0.0067	0.0001	0.0012	0.0011	0.0029	0.0001	0.0004	0.0003	0.0004	0.0004	0.0026
RSD		1.1	2.2	2.5	1.9	3.6	4.7	2.1	2.1	6.2	0.5	39.8	7.4	1.2	10.8	3.9
Świbie 72a	<LOD	0.002	0.003	0.0131	<LOD	0.0081	<LOD	<0.004	0.0001	0.001	<LOD	0.001	<LOD	<LOD	0.0005	0.002
RSD		3.8	20.3	4.5		13.9			6.0	10.1		29.2			5.9	7.5
Świbie 74a	<LOD	0.0023	0.0027	0.0137	0.0009	0.011	0.0003	0.0016	0.0008	0.0015	0.0002	0.0002	0.0002	0.0003	0.0046	0.0023
RSD		15.1	5.5	13.1	21.6	2.9	13.4	42.6	21.6	24.6	5.5	6.9	20.7	4.6	9.5	12.6
Świbie 77	<LOD	0.001	0.002	0.0139	0.001	0.008	0.001	<0.002	0.001	0.001	<0.001	<LOD	<LOD	0.0001	0.0005	0.001
RSD		4.9	22.0	6.1	5.3	4.7	16.9		6.9	2.0				10.1	11.3	14.3
Other																
Świbie 78	<LOD	0.001	0.002	0.0245	<LOD	0.0059	0.001	0.0137	<LOD	0.001	<LOD	0.001	<LOD	<LOD	0.0014	0.002
RSD		3.9	13.5	3.8		5.1	7.7	24.4		9.5		10.1			6.8	8.6

Table 3
Chemical composition of the glass of the ornament decorating beads made of glassy faience (oxides wt%) and relative standard deviation values (RSD, %) obtained with LA-ICPMS (abbreviations: <LOD = below the limit of detection of the method).

Site and sample no.	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3	MnO	Sb_2O_5	PbO	CoO	CuO	BaO	TiO_2	SnO_2	NiO	ZnO	As_2O_5	P_2O_5	B_2O_3
LOD	0.1030	0.0001	0.0002	0.0092	0.0006	0.0002	0.0015	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0005	0.0001	0.0023	0.0003	0.0002	0.0016	0.0007
Domasław 8b	54.94	13.13	0.25	2.98	0.37	0.47	0.85	0.21	0.95	24.99	<LOD	0.01	0.004	0.13	<LOD	<LOD	0.002	0.003	0.03	0.05
RSD	0.6	1.2	11.4	1.8	0.6	1.6	1.8	1.2	7.9	1.6		10.3	2.1	0.8			12.3	5.6	6.1	3.5
Domasław 18b	27.28	6.93	0.05	0.42	0.16	0.35	1.57	0.01	2.39	60.43	<LOD	0.03	0.003	0.04	0.001	<0.006	0.001	0.01	0.04	0.02
RSD	3.0	7.4	2.5	2.1	3.3	3.4	3.3	0.4	10.3	2.0		31.9	39.5	4.3	5.4		2.7	3.9	40.9	3.6
Gorszewice 24b	39.68	8.52	0.26	1.62	0.25	0.73	2.08	0.02	3.05	42.55	<0.003	<0.28	<0.01	0.08	<0.01	<LOD	<0.02	0.17	<0.16	0.03
RSD	6.1	6.7	34.1	2.9	4.1	19.7	29.4	4.7	13.0	2.8				17.2				15.7		4.4
Gorszewice 25b	48.98	12.80	0.42	1.49	0.37	0.72	1.66	0.02	1.49	29.58	0.001	0.09	0.004	0.05	<LOD	0.001	0.003	1.26	<0.11	0.05
RSD	6.4	8.1	7.6	4.5	8.4	8.7	4.6	6.8	6.3	11.8	17.0	19.2	24.7	7.9		15.7	34.4	6.6		2.4
Gorszewice 26b	50.58	11.03	0.33	1.83	0.29	0.72	1.90	0.03	2.42	29.67	<LOD	0.03	<0.004	0.09	0.001	0.001	0.003	0.20	0.03	0.04
RSD	13.4	8.8	14.4	5.6	6.8	6.9	9.0	4.9	19.4	9.0		7.4		7.9	18.8	38.9	25.4	10.6	32.7	4.6
Kraków-Bieżanów 46b	54.51	13.14	0.20	2.02	0.54	1.02	3.14	0.02	1.31	22.55	0.0003	0.02	0.003	0.07	0.0002	<0.0037	0.002	0.35	0.02	0.07
RSD	0.9	1.7	2.5	0.4	0.8	1.2	1.8	1.6	6.7	2.3	6.8	2.3	2.3	3.0	7.8		11.6	3.0	4.5	2.4
Świbie 68b	51.01	11.43	0.19	1.91	0.36	0.54	1.49	0.01	1.71	23.31	0.0002	0.01	0.003	0.09	0.0002	<0.0026	0.002	0.01	0.02	0.07
RSD	1.4	4.9	9.9	6.4	6.3	1.5	11.8	13.7	4.2	0.2	26.7	24.4	9.9	4.6	16.2		10.3	2.3	5.6	1.5
Świbie 69b	52.38	7.07	0.23	1.06	0.28	0.81	3.57	0.02	1.55	30.19	0.0002	0.05	0.003	0.04	0.0281	<0.0026	0.01	1.71	0.08	0.05
RSD	1.5	2.2	7.2	1.2	2.3	4.1	4.6	3.1	7.1	2.0	1.5	12.6	12.1	7.2	14.9		28.9	4.2	29.5	6.4
Świbie 76b	50.04	11.45	0.23	1.92	0.52	0.91	3.30	0.02	1.65	28.80	0.0003	0.02	0.003	0.06	0.0004	<LOD	0.002	0.33	0.02	0.07
RSD	2.9	7.8	4.2	0.7	2.6	2.2	2.1	1.1	3.4	1.8	1.9	26.3	1.3	0.5	11.5		10.1	0.6	2.1	4.6

Site and sample no.	Cs_2O	V_2O_5	Rb_2O	SrO	Y_2O_3	ZrO_2	MoO_2	Ag_2O	La_2O_3	Ce_2O_3	HfO_2	Bi_2O_3	ThO_2	UO_2	Li_2O	Cr_2O_3
LOD	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0004
Domasław 8b	<LOD	0.003	<LOD	0.0131	<LOD	0.0121	<LOD	0.001	<LOD	0.002	<LOD	<LOD	<LOD	<LOD	0.0005	0.002
RSD		1.3		2.0		1.8		6.6		1.5					11.1	2.9
Domasław 18b	<LOD	0.001	<LOD	0.0041	<LOD	0.002	<LOD	0.0051	<LOD	0.001	<LOD	0.002	<LOD	<LOD	0.0005	0.001
RSD		8.8		2.6		0.5		1.6		3.1		7.3			5.8	26.8
Gorszewice 24b	<LOD	0.002	<0.001	0.0051	0.001	0.0051	<LOD	0.0051	<0.001	0.001	<LOD	0.002	<LOD	<LOD	0.001	0.0031
RSD		30.2		6.7	46.2	5.2		18.6		33.1		27.0			43.3	27.1
Gorszewice 25b	<LOD	0.002	0.001	0.0061	<LOD	0.002	<LOD	0.0061	<LOD	<LOD	<LOD	<0.0001	<LOD	<LOD	0.001	0.0041
RSD		6.4	15.4	24.7		9.3		6.7	3.2	5.7					14.2	13.8
Gorszewice 26b	<LOD	0.0021	0.001	0.0063	0.001	0.0063	<LOD	0.0063	0.001	0.001	<LOD	0.0021	<LOD	<LOD	0.0005	0.0021
RSD		6.1	26.2	7.0	6.4	6.8		6.3	6.3	9.9		13.0			10.6	3.2
Kraków-Bieżanów 46b	<LOD	0.0021	0.0003	0.0087	0.0003	0.0025	0.0001	0.0049	0.0003	0.0005	<LOD	0.0001	0.0001	0.0003	0.0004	0.0032
RSD		3.4	6.2	1.1	3.3	4.3	1.6	0.7	0.9	4.7		1.2	1.0	3.5	9.7	3.3
Świbie 68b	<LOD	0.0017	0.0002	0.0095	0.0003	0.0079	0.0002	0.002	0.0003	0.0006	0.0002	<LOD	0.0001	0.0002	0.0005	0.001
RSD		2.5	16.9	9.9	5.0	4.8	15.0	10.5	10.7	9.1	9.7		9.2	6.9	15.2	11.3
Świbie 69b	<LOD	0.0017	0.0004	0.0039	0.0003	0.0016	0.0001	0.0075	0.0002	0.0004	<LOD	0.0002	0.0001	0.0003	0.0002	0.0035
RSD		6.4	9.2	0.9	9.7	3.3	5.3	6.8	5.5	10.4		3.1	0.9	4.4	13.6	1.5
Świbie 76b	<LOD	0.0019	0.0004	0.008	0.0003	0.0027	0.0001	0.0051	0.0003	0.0005	0.0001	<LOD	0.0001	0.0003	0.0007	0.0034
RSD		2.9	15.2	2.7	1.2	2.2	32.8	2.8	6.0	2.0	17.5		7.1	1.2	3.9	5.1

Table 4
LA-ICPMS operating conditions.

LA characteristics and settings	
Wavelength, nm	213
Energy, mJ	4.5
Ablation mode	Single point
Beam diameter, μm	100
Repetition rate, Hz	10
ICPMS characteristics and settings	
RF Power, W	1045
Carrier gas (Ar) flow rate, L min^{-1}	1
Sweeps	1
Readings	251
Replicates	1
Dwell time, ms	10

compounds were observed in non-transparent LMMK glass of brownish-red color (sample no. 73a).

3.2.2. True glass – LMG glass

LMG true glass of yellow color used for the decoration appearing on the beads revealed – compared to the LMMK and LMG_{GF} glass of glassy faience – a low concentration of K_2O (0.05%–0.42%) and SiO_2 (27.28%–54.94%), but very high PbO (22.55%–60.43%) and Sb_2O_5 (0.95%–3.05%) instead (Fig. 9). LMG true glass, like the LMG_{GF} glass in glassy faience, has low levels of Na_2O (6.93%–13.14%), MgO (0.16%–0.54%) and most trace elements, including Ti (≤0.13% TiO_2) and B (≤0.07% B_2O_3) (Fig. 9). Similarly to LMMK and LMG_{GF} glasses in glassy faience, LMG true glass has a low content of CaO (0.42%–2.98%). The level of Al_2O_3 (0.35%–1.02%) is on the whole lower than in glasses forming glassy faience, whereas Fe_2O_3 (0.85%–3.57%) was recorded at a similar or slightly lower level. Cobalt was not found and CuO appeared in a small concentration.

4. Discussion

4.1. Glassy faience – LMMK and LMG_{GF} glass

The alkali composition of the analyzed samples allows the LMG_{GF} glass to be classified as glass produced with natron as flux. The soda used in the production of LMMK glass cannot be easily identified as either natron or plant ash, because the composition of these glasses is unusual: a mean content of K_2O (higher than in LMG glass from the Early Iron Age, but lower than in LMHK glass from the Final Bronze Age) and low content of MgO. Glasses from Italy with a similar concentration of potassium and magnesium have been interpreted differently. Towle and Henderson (2007: 51, 57, Table 5:177, 178) attributed such glasses (2.6% or 1.89% K_2O and 1.01% or 1.05% MgO) to low magnesia (natron) soda-lime–silica glass. Arletti et al. (2010: 709) determined that the glass of sample no. IG11b (3.44% K_2O and 1.32% MgO) was probably melted from very different raw materials and cannot be classified as glass produced with natron. On the other hand, Santropadre and Verità (2000: 29, Table 1, sample C1) considered the glass in glassy faience (4.60% K_2O and 0.30% MgO) to represent a *mixed alkali* group. Reade et al. (2009: 49, 52) did not rule out the possibility that plant ash with small amounts of potash, magnesia and lime was utilized in the making of LMLK glass from Pella in Jordan, which is occasionally characterized by content of K_2O or MgO less than 2%. These examples reveal the difficulty of determining the raw material used as flux in the production of glasses containing mean amounts of K_2O and little MgO. Henderson (2013: 94) opined that LMMK were probably natron glasses, and the higher levels of potassium could have been due to sand containing potassium feldspar. BSE images of glassy faience from Poland show isolated grains of potassium feldspar in only five instances (Purowski, 2012: Figs. 35k, 40b, 48d; Purowski et al., 2012: 159); these glasses are not distinguished by the highest levels of potassium, containing from 1.5% to 2.2% K_2O. Perhaps halophyte plant ash was indeed used in the production of LMMK glass (with concentrations of about 2%–3% K_2O, and occasionally 5% K_2O). Lower MgO levels (frequent in halophyte plants; Barkoudah and Henderson, 2006) in LMMK glass could be explained, as in the case of LMHK glass from the Final Bronze Age, by the use of a specific alkali raw material (e.g., mixture of local continental and maritime plants) or special treatment (e.g., leached plant ash), which could have caused lowered magnesium in the plant ash (cf. Venclová et al., 2011: 577). Neither can it be ruled out that the plant ash used contained low concentrations of magnesium compounds.

Observation of phosphorus content failed to throw light on the issue of the raw material (whether natron or plant ash) that was used for producing LMMK glass. In the opinion of Hartmann et al. (1997: 552), higher P_2O_5 concentrations in glass are evidence for the use of plant ash in the glass manufacturing process. P_2O_5 in LMMK glass (with the exception of sample no. 73a) falls in the range of 0.09%–0.22%, which is neither high nor low. Moreover, the content of P_2O_5 in LMG_{GF} glass produced most likely with natron, was observed frequently at the same level or sometimes higher.

Other elements which could have been introduced with the sand beside silica include aluminum, iron and some of the trace elements (boron, barium, titanium, zircon and others). High Al_2O_3 suggests the use of sand, which was very rich in the feldspathic component, in the production of LMMK (Arletti et al., 2010: 710). Therefore, potassium feldspar may have been a source of not only potash compounds, but also silicon and aluminum. Sand used to melt LMG_{GF} presumably had a different chemical composition with less aluminum. Different amounts of this element in LMMK and LMG_{GF} glass of blue color could demonstrate that the high level of Al_2O_3 in LMMK glass was not due to the adding of a colorant containing cobalt (see below).

The relatively large amounts of barium compounds in the LMMK glass composition could have entered presumably together with feldspars present in sand (cf. Silvestri, 2008: 1498; Panighello et al., 2012: 2950). Higher amounts of trace elements, like boron and titanium compounds, in this group could have had the same source, that is, sand. As shown in Figs. 10 and 11, B_2O_3 and TiO_2 content in LMMK glass is well correlated with Al_2O_3. Titanium is also well correlated with boron (Fig. 8), but not with iron (iron compounds may have come also from sources other than the sand, see below). Neuninger and Pittioni (1959: 61 and note 23) observed that boric acid occurred in Italy near the volcanoes in the form of a mineral (sassolite). Titanium is a frequent impurity in some sands (Nowotny, 1959: 230; Henderson, 1985: 271; Arletti et al., 2011: 2097). These compounds each played a different role in the glass. Boron oxide in amounts of 0.5% has a positive impact on the product and utilitarian properties of the glass, improving melting ease, lowering viscosity and increasing chemical resistance (Nowotny, 1959: 242). Titanium is not beneficial to the optical properties of glass, because it intensifies the color imparted to on the glass mass by iron compounds (Nowotny, 1959: 230). Neuninger and Pittioni (1959: 61–62) stated that glasses with boron added were first produced in Europe in the Hallstatt A phase in northern Italy and later also in neighboring territories. Most frequently, B_2O_3 in Egyptian or Near Eastern glass does not exceed 0.05%; slightly higher concentrations (≤0.5%) were observed in glass from Hasanlu, dated from c. 1100 to 800 BC (Brill, 1999).

Zircon in LMMK glass is well correlated with aluminum (Fig. 12), titanium (Fig 13), boron and strontium (Fig. 14). SrO in ancient glass is mainly associated with the lime-bearing material, limestone or

Table 5
Major, minor and trace element oxide composition of Corning B and Corning D determined by different authors. RSD values in percents are given in brackets.

	Li_2O	B_2O_3	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	V_2O_5	Cr_2O_3	MnO	Fe_2O_3
Corning B														
Values determined in this work	0.005 (8.9)	0.035 (5.6)	15.98 (1.1)	0.916 (3.1)	3.910 (0.7)	63.00 (0.2)	0.428 (1.4)	1.036 (2.6)	8.793 (0.5)	0.100 (1.0)	0.033 (0.4)	0.009 (1.4)	0.226 (1.4)	0.332 (1.6)
Wagner et al. (2012)	0.003 (4.6)	0.036 (6.4)	16.5 (0.5)	0.988 (0.7)	4.63 (1.3)	62.02 (0.3)	0.611 (0.8)	1.30 (1.4)	8.75 (1.4)	0.099 (1.9)	0.034 (1.2)	0.010 (3.1)	0.241 (1.2)	0.311 (1.5)
Dussubieux et al. (2009)			15.4 (1.2)	1.04 (0.08)	4.74 (0.26)	63.8 (0.7)	0.60 (0.21)	1.03 (0.12)	1.13 (0.27)	0.10 (0.02)	0.031 (0.002)		0.22 (0.01)	0.27 (0.01)
Brill (1999)			17.0	1.03	4.36	61.55	0.82	1.00	8.56	0.089			0.25	0.34
Brill (1972)	0.005	0.02	17.2	1.12	4.21	61.5	0.90	1.06	8.69	0.13	0.03	0.005	0.25	0.37
Corning D														
Values determined in this work	0.012 (6.0)	0.103 (4.8)	1.148 (0.5)	3.468 (1.0)	5.596 (1.2)	54.02 (0.6)	2.221 (2.0)	13.99 (1.3)	15.49 (1.1)	0.396 (1.0)	0.018 (0.5)	0.003 (6.9)	0.495 (0.9)	0.501 (1.6)
Wagner et al. (2012)	0.006 (1.3)	0.105 (3.0)	1.30 (1.4)	3.87 (1.3)	5.19 (3.0)	58.36 (1.2)	3.05 (0.9)	14.2 (0.7)	14.7 (2.4)	0.356 (2.7)	0.017 (1.1)	0.003 (4.1)	0.597 (1.1)	0.460 (2.1)
Dussubieux et al. (2009)			1.65 (0.35)	3.76 (0.31)	5.96 (0.14)	56.5 (1.0)	3.07 (0.85)	9.39 (0.56)	16.0 (1.4)	0.39 (0.11)	0.017 (0.001)		0.557 (0.007)	0.41 (0.01)
Brill (1999)			1.20	3.94	5.30	55.24	3.93	11.3	14.8	0.38			0.55	0.52
Brill (1972)	0.005	0.10	1.39	4.06	5.42	55.1	3.50	11.56	14.99	0.39	0.02	0.002	0.55	0.51

	CoO	NiO	CuO	ZnO	Rb_2O	SrO	ZrO_2	Ag_2O	SnO_2	Sb_2O_5	BaO	PbO	Bi_2O_3
Corning B													
Values determined in this work	0.043 (2.6)	0.088 (4.3)	2.609 (1.2)	0.252 (1.9)	0.001 (1.6)	0.018 (2.4)	0.025 (1.6)	0.008 (3.2)	0.027 (2.6)	0.464 (1.6)	0.076 (1.6)	0.564 (1.0)	0.005 (0.8)
Wagner et al. (2012)	0.043 (0.8)	0.094 (1.1)	2.82 (1.7)	0.211 (1.7)	0.001 (2.3)	0.017 (1.9)	0.023 (2.7)		0.024 (0.9)	0.418 (1.8)	0.077 (2.5)	0.532 (2.5)	0.004 (2.4)
Dussubieux et al. (2009)		0.082 (0.008)	2.31 (0.17)	0.17 (0.03)		0.0167 (0.0003)			0.021 (0.001)	0.45 (0.07)	0.08 (0.02)	0.45 (0.04)	
Brill (1999)	0.046		2.66	0.19		0.019			0.04	0.46	0.12	0.61	
Brill (1972)	0.04	0.10	2.68	0.20	0.001	0.02	0.025	0.01	0.03	0.45	0.10	0.50	0.005
Corning D													
Values determined in this work	0.018 (0.5)	0.043 (3.6)	0.357 (1.0)	0.126 (3.5)	0.005 (3.5)	0.062 (1.1)	0.014 (1.9)	0.004 (2.8)	0.097 (1.6)	0.962 (1.7)	0.303 (1.5)	0.287 (1.3)	0.002 (0.8)
Wagner et al. (2012)	0.018 (1.3)	0.048 (1.4)	0.370 (1.6)	0.102 (1.6)	0.005 (2.0)	0.055 (2.6)	0.011 (4.9)		0.084 (1.9)	0.961 (1.9)	0.291 (1.8)	0.241 (1.4)	0.001 (3.7)
Dussubieux et al. (2009)		0.046 (0.05)	0.37 (0.7)	0.090 (0.007)		0.065 (0.001)			0.08 (0.01)	0.96 (0.09)	0.38 (0.09)	0.23 (0.01)	
Brill (1999)	0.023		0.38	0.10		0.057			0.10	0.97	0.51	0.48	
Brill (1972)	0.02	0.06	0.38	0.10	0.005	0.05	0.01	0.005	0.15	0.98	0.33	0.25	0.002

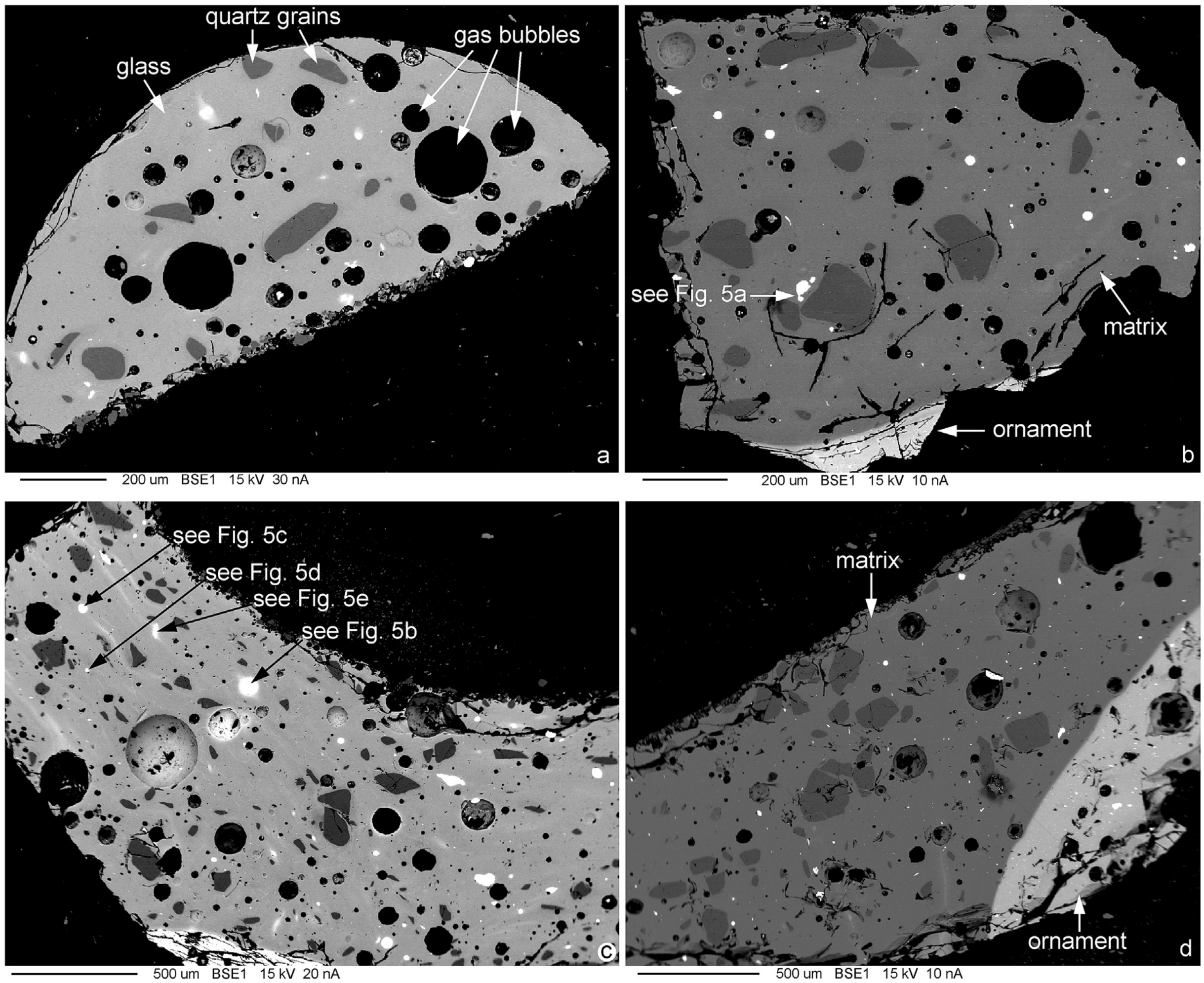

Fig. 4. Backscattered electron images of beads: (a) Domasław, sample 16; (b) Orzech, sample 50; (c) Domasław, sample 19; (d) Domasław, sample 8.

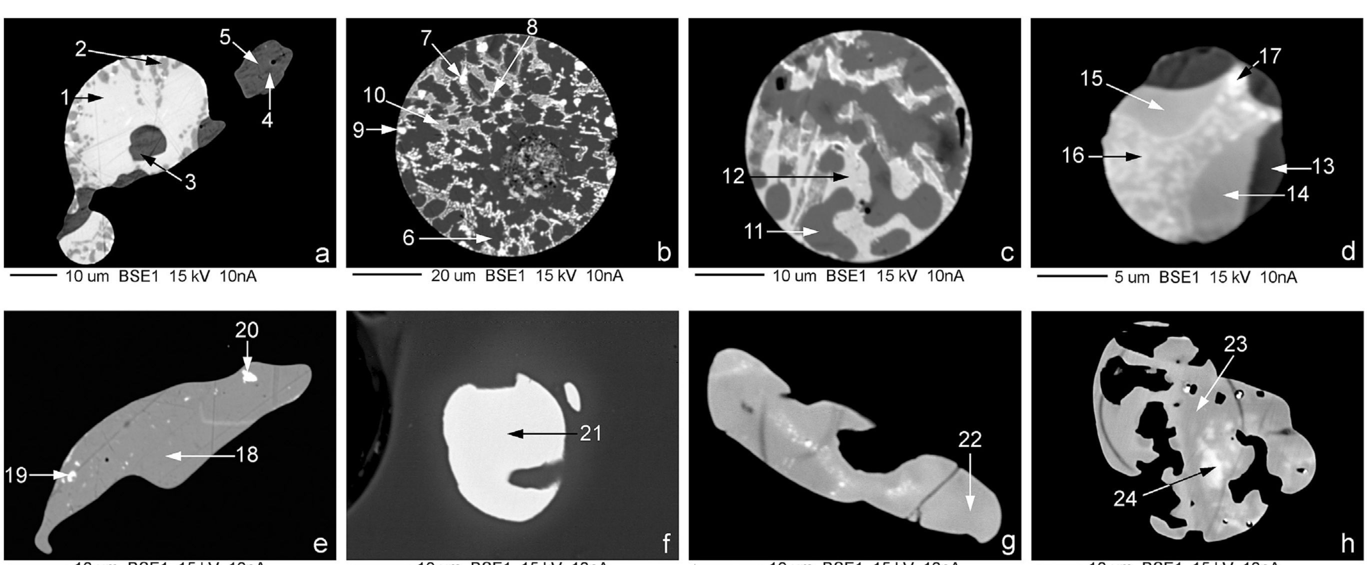

Fig. 5. Backscattered electron images of beads: (a) Orzech, sample 50a; (b–e) Domasław, sample 19a; (f) Domasław, sample 15; (g–h) Domasław, sample 18a; (1–20) numbers of analyses from Table 6; (21–24) numbers of analyses from Table 7.

Table 6
Chemical composition of inclusions in the glass of glassy faience (wt%), presented in Fig. 5a–e, obtained with EPMA (abbreviations: <LOD = below the limit of detection of the method).

Site and sample no.	Orzech 50a					Domasław 19a														
Analysis no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Fe	0.10	0.19	0.08	0.18	0.22	0.29	<LOD	<LOD	0.20	<LOD	0.77	0.29	0.49	0.40	0.45	0.49	0.33	0.32	0.31	0.28
Sb	20.38	2.15	0.19	<LOD	<LOD	<LOD	0.86	<LOD	0.51	<LOD	<LOD	<LOD	0.39	11.73	11.78	17.36	7.49	<LOD	<LOD	0.23
Pb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	95.62	75.53	84.57	41.31	<LOD	38.82	<LOD	<LOD	<LOD	1.35	7.62	<LOD	48.13	63.63
Co	<LOD	<LOD	<LOD	0.08	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.26	<LOD	<LOD	0.22	0.24	1.01	0.76	<LOD	0.32	<LOD
Cu	46.65	86.92	78.55	77.79	77.44	79.65	5.63	7.96	4.09	42.33	76.66	43.06	76.61	33.51	35.07	18.54	3.06	77.08	22.52	12.39
Sn	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ni	14.24	1.58	0.22	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.33	<LOD	1.05	22.60	22.77	25.52	8.85	<LOD	5.75	2.20
Zn	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ag	<LOD	1.31	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.42	57.00	3.77	0.45	0.43
As	18.00	6.06	0.35	0.32	0.31	<LOD	<LOD	<LOD	<LOD	0.25	<LOD	<LOD	0.28	26.02	26.52	29.45	9.94	<LOD	<LOD	<LOD
S	<LOD	<LOD	18.92	19.20	19.09	20.49	0.75	13.87	10.84	16.74	21.62	17.29	19.34	<LOD	<LOD	0.21	0.38	20.28	17.29	14.69
Total	99.38	98.22	98.35	97.61	97.05	100.43	102.85	97.35	100.22	100.63	99.65	99.46	98.17	94.48	96.83	94.37	95.43	101.45	94.76	93.85

Table 7
Chemical composition of inclusions in the glass of glassy faience (oxides wt%), presented in Fig. 5f–h, obtained with EPMA (abbreviations: <LOD = below the limit of detection of the method; n.a. = not analyzed).

Site and sample no.	Domasław 15	Domasław 18a		
Analysis no.	21	22	23	24
SiO_2	0.61	<LOD	<LOD	<LOD
CaO	<LOD	<LOD	<LOD	<LOD
MgO	0.60	0.93	0.87	1.33
Al_2O_3	2.97	1.98	1.75	1.59
Fe_2O_3 [a]	63.97	61.36	60.48	52.09
FeO [a]	23.74	2.66	2.87	<LOD
MnO	<LOD	<LOD	<LOD	<LOD
NiO	1.65	14.26	13.16	15.17
Sb_2O_5	n.a.	0.40	<LOD	<LOD
CoO	5.11	10.65	11.60	12.96
CuO	n.a.	1.51	1.69	1.13
TiO_2	0.37	<LOD	<LOD	<LOD
SnO_2	0.28	3.58	6.26	16.96
Total	99.30	97.33	98.68	101.23

[a] Iron classification by valence based on recalculation of analyses results into a chemical formula of spinel assuming 32 oxygen atoms in an elementary cell.

plant ash. Glass produced using Mediterranean coastal sand has typically low ZrO_2 (<0.01%) and high SrO (>0.03%) content due to the aragonite of the shells in beach sand. Glass made from inland sand, containing calcium carbonate derived from limestone, contains less SrO (<0.02%) and more ZrO_2 (>0.015%) (e.g., Freestone et al., 2003; Silvestri, 2008; Panighello et al., 2012 and references therein). Nearly all LMMK glass has SrO < 0.02% and ZrO_2 > 0.015%, whereas LMG_{GF} glass have less SrO (<0.015%) and ZrO_2 (<0.016%). The data in Figs. 14 and 15 seem to indicate that at least LMMK glass was made from inland sand.

As shown in Figs. 8 and 10–15 the ratio of components in LMG_{GF} glasses is different than in LMMK glasses, indicating that it was melted from raw material of slightly different chemical composition extracted from different places. Iron compounds are frequent as impurities in the sand. High levels of Fe_2O_3 in LMMK and LMG_{GF} glass could be proof that it was introduced into the glass not only with the sand (Arletti et al., 2012: 3399). It could have come, for example, with the lead compounds (cf. Arletti et al., 2010: 711) or colorant-rich minerals (Venclová et al., 2011: 575).

One should note the high content of PbO and Sb_2O_5 in blue and brownish-red glasses. They had no role in the opacity of the glass. Lead may have been added to improve the fluidity of the melt (cf. Arletti et al., 2010: 711).

Iron (7.38% Fe_2O_3) and copper (1.34% CuO) compounds probably had the greatest influence on the color of brownish-red glass (sample no. 73a). Blue glasses owed their color foremost to cobalt

Table 8
Chemical composition of inclusions found in the glass of the ornament (oxides wt%), obtained with EPMA (abbreviations: <LOD = below the limit of detection of the method).

Site and sample no.	Domasław 18b		
Analysis no.	25	26	27
SiO_2	2.14	2.13	1.72
Na_2O	0.76	0.44	0.30
CaO	<LOD	<LOD	<LOD
MgO	<LOD	<LOD	<LOD
Al_2O_3	<LOD	<LOD	<LOD
Fe_2O_3	6.47	6.28	5.95
Sb_2O_5	34.04	30.70	30.44
PbO	56.01	59.00	59.45
As_2O_5	0.53	0.46	0.52
Total	99.3	98.38	97.78

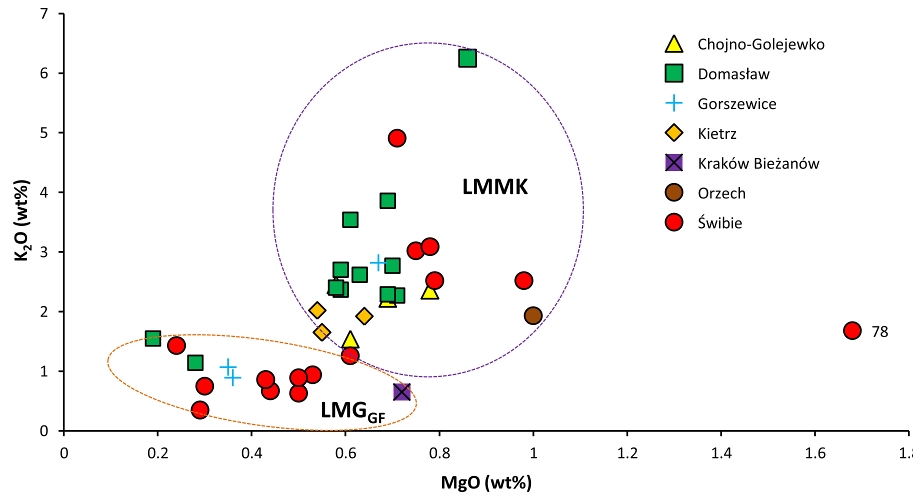

Fig. 6. K_2O versus MgO in the glass of glassy faience determined by LA-ICPMS method.

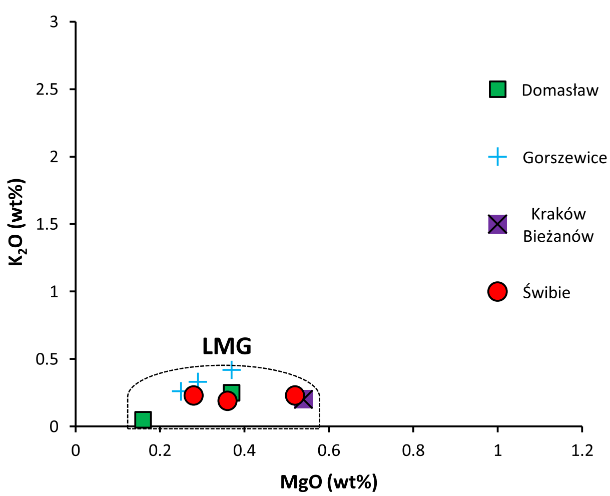

Fig. 7. K_2O versus MgO in true glass determined by LA-ICPMS method.

compounds (0.11%–0.82% CoO). Even small amounts (>0.005% CoO) can color glass blue (Bachtadze et al., 2002: Table 3). Numerous studies have been aimed at tracing the source of cobalt in glass (e.g., Shortland and Tite, 2000; Rehren, 2001; Gratuze, 2009; Arletti et al., 2010; Abe et al., 2012). The presence of cobalt in all Egyptian vitreous materials of the New Kingdom is strongly associated with raised levels of other elements, chiefly aluminum, magnesia, manganese, nickel and zinc (Shortland and Tite, 2000: 145). Alum is presumed to have been the source of cobalt in these glasses. Higher levels of MgO were not observed in blue glass of glassy faience from the Halstatt period from sites in Poland despite the fact that CoO is higher in them (average 0.34%) than in glasses from Amarna, for example (average 0.17%) analyzed by Shortland and Tite (2000: 145). Glasses from Poland also do not demonstrate a correlation between the amounts of CoO and Al_2O_3, because high concentrations of cobalt (>0.6% CoO) were observed in glasses with low as well as high aluminum content (e.g., 0.85% Al_2O_3 in sample no. 12a and 8.1% Al_2O_3 in sample no. 64). The glasses from the studied collection also have lower magnesium content compared to the aluminum–magnesium glasses colored with cobalt (from alum presumably) found in French sites from the

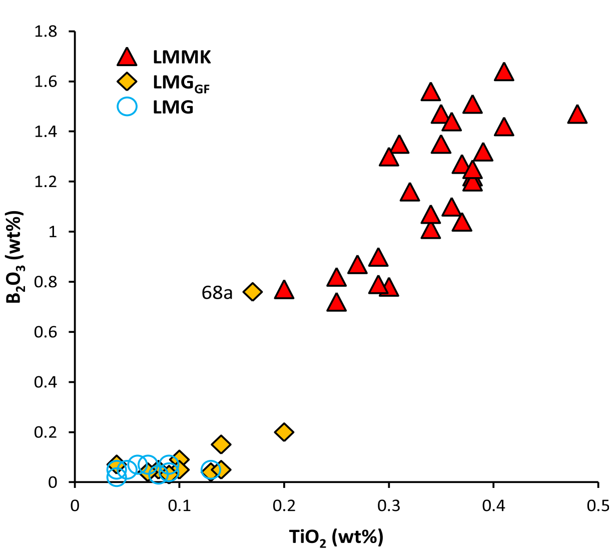

Fig. 8. TiO_2 versus B_2O_3 for the analyzed samples (LA-ICPMS).

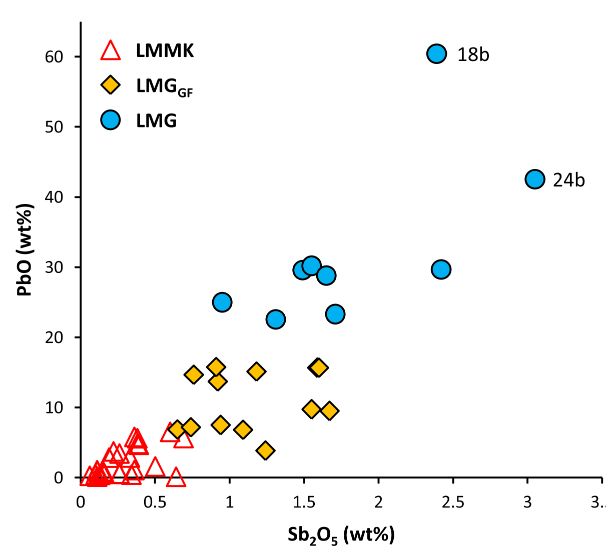

Fig. 9. Sb_2O_5 versus PbO for the analyzed samples (LA-ICPMS).

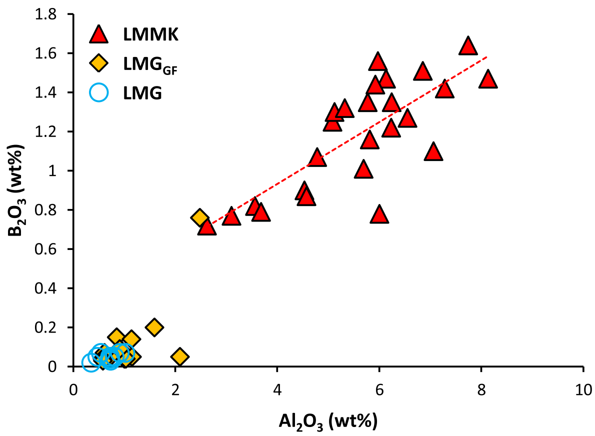

Fig. 10. Al_2O_3 versus B_2O_3 for the analyzed samples (LA-ICPMS).

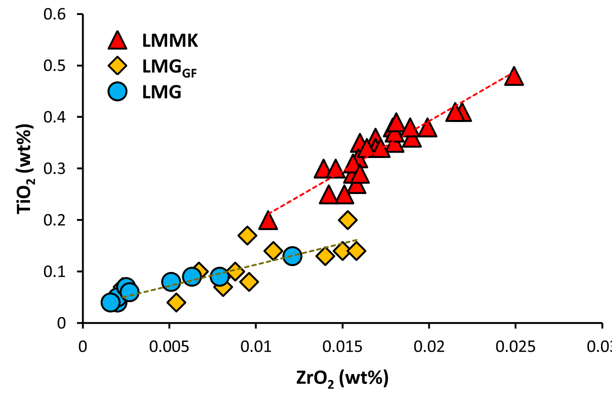

Fig. 13. ZrO_2 versus TiO_2 for the analyzed samples (LA-ICPMS).

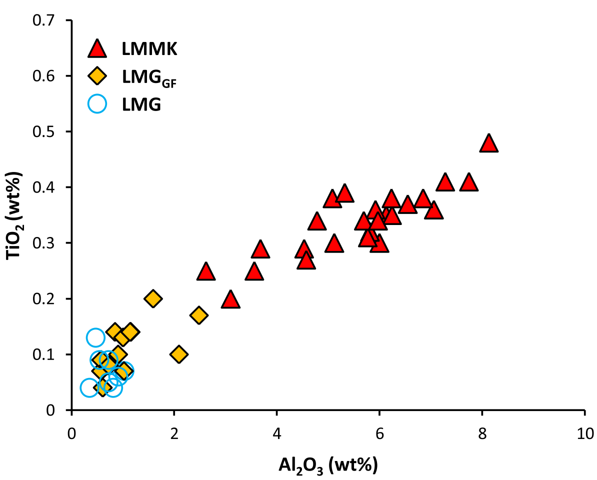

Fig. 11. Al_2O_3 versus TiO_2 for the analyzed samples (LA-ICPMS).

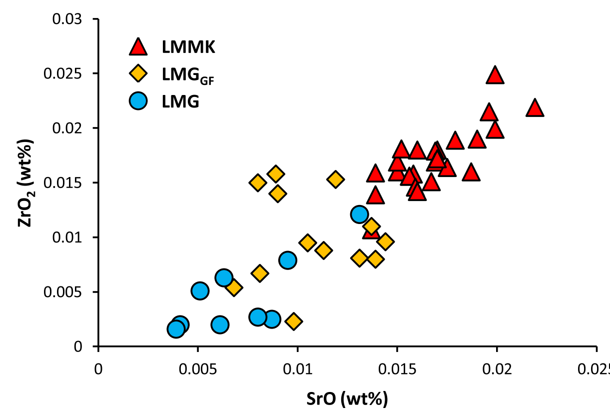

Fig. 14. SrO versus ZrO_2 for the analyzed samples (LA-ICPMS).

Iron Age (Gratuze, 2009). The evident connection between concentrations of CoO and the content of MnO, observed in Mediterranean Group II from the Iron Age (Arletti et al., 2011: 2099) was not observed here. An association does exist, however, between levels of CoO and NiO. As shown in Fig. 16, cobalt and nickel are linearly correlated, but with two different slopes. On top of that, inclusions, made up of Co, Ni and Fe among others, identified in the glassy faience from Poland appear to indicate that the raw material used in its production contained cobalt and nickel, as well as other components, such as iron. The use of cobalt minerals could lead to the introduction into the glass of, among others, Fe, Ni, As, S, Mn, but also Pb, Sb, Zn (Koch, 2011: 25). It cannot be ruled out that this raw material originated from Europe, because cobalt minerals are common in modern Germany, Austria, Switzerland, the Czech Republic and Slovakia (Henderson, 1985: 280). Similar cobalt and nickel content has been observed in some black glass from Hallstatt C from Croatia and Hungary, as well as blue glass from the Bronze

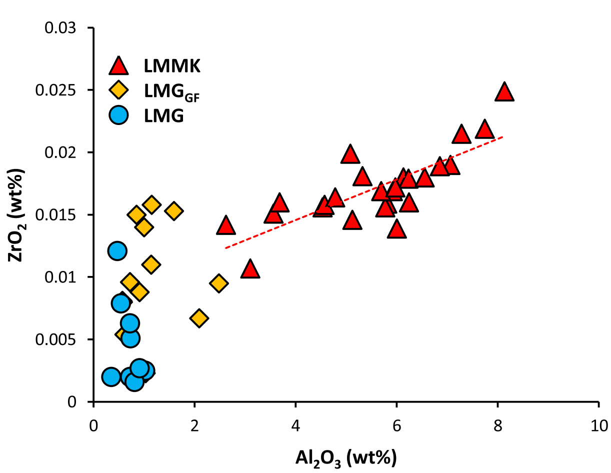

Fig. 12. Al_2O_3 versus ZrO_2 for the analyzed samples (LA-ICPMS).

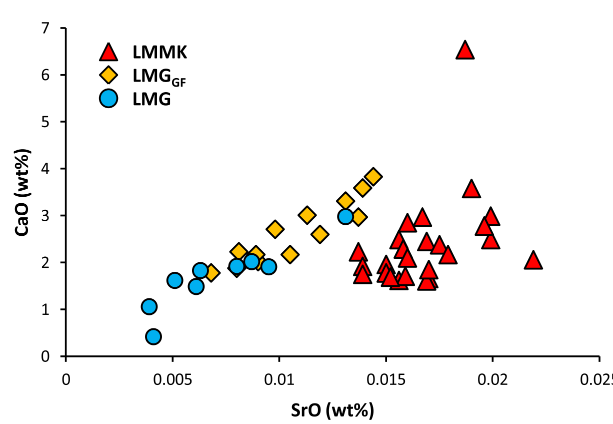

Fig. 15. SrO versus CaO for the analyzed samples (LA-ICPMS).

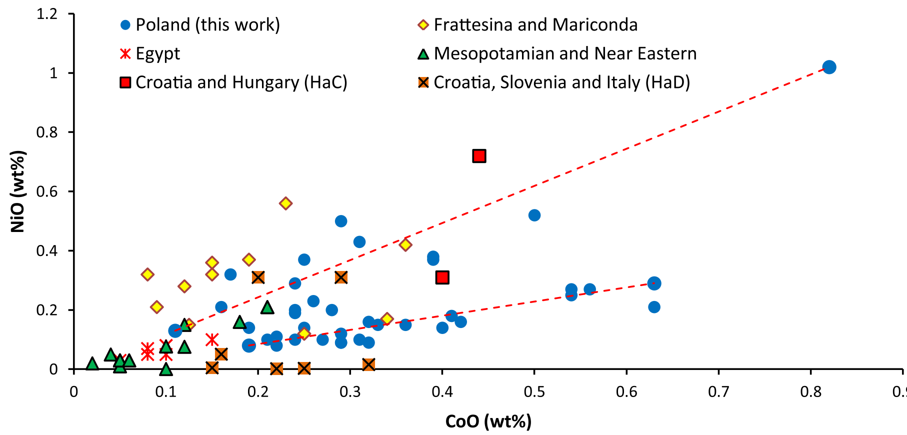

Fig. 16. CoO versus NiO for the analyzed samples of glassy faience (LA-ICPMS) compared to other Bronze Age and Early Iron Age glasses. Frattesina and Mariconda from Towle et al. (2001) and Brill (1999), Egyptian, Mesopotamian and Near Eastern from Brill (1999), Croatian and Hungarian (Hallstatt C) and Croatian, Slovenian and Italian (Hallstatt D) from Braun (1983).

Age from Mariconda and Frattesina in Italy (Fig. 16). With regard to the latter glasses, the cobalt may have issued from sources in Central Europe (Towle et al., 2001: 24). Dark blue Egyptian, Mesopotamian and Near Eastern glass from the 2nd and first half of the 1st millennium BC usually have much lower CoO and NiO content.

4.2. True glass – LMG glass

The low contents of K_2O, MgO and P_2O_5 in opaque glass of yellow color point to the use of mineral soda in its production (e.g., Hartmann et al., 1997: 552). Sand used in the process of manufacturing LMG glass contained small amounts of aluminum and trace elements, compared with the LMMK and LMG_{GF} of this study. Iron got into the glass not only with the sand, but presumably also with the opacifier–colorant raw material. LMG glass has been observed to have relatively high content of Fe_2O_3 and Sb_2O_5 and very high levels of PbO (Fig. 9). They were opacified and colored with lead antimonate $Pb_2Sb_2O_7$ (cf. Henderson, 2000: 27; Purowski et al., 2012: 163), which has been confirmed in BSE images showing numerous inclusions in the glass, composed principally of lead and antimony and to a lesser extent of iron. The lack of other colorants in the glass suggests that lead antimonate was added to colorless glass.

Research to date has demonstrated the use of $Pb_2Sb_2O_7$ for producing yellow opaque glass virtually from the beginning of glass production (about 1500 BC) through the Roman period (Turner and Rooksby, 1959; Tite et al., 2008: 67). According to Shortland (2002: 524), lead antimonate is seldom encountered in a natural state, so it must have been formed artificially by the combination of lead and antimony ore minerals. The technique for forming lead antimonate has yet to be satisfactorily explained. Certain researchers have suggested that $Pb_2Sb_2O_7$ was obtained by adding a combination of roasted lead and antimony ore minerals to the glass batch, thus producing oxides, the lead being in excess (e.g., Shortland, 2002; Arletti et al., 2010: 711, 2012: 3400).

5. Conclusions

Objects made of glassy materials commonly used in Central Europe in the second half of the 8th through 7th centuries BC were made for the most part of glassy faience and not true glass. Formal parallels for beads discussed in the present study indicate that in all likelihood the beads were made in Italy and/or in the regions of Slovenia and Croatia (Purowski, 2012). Confirmation of the idea by physico-chemical analyses will be possible only after numerous analytical studies of glassy faience from the region are made. For now it can be said that objects of glassy faience were produced most likely in Europe, because Egyptian and Near Eastern glass have a slightly different chemical composition (e.g., they contain more CaO).

During Hallstatt C no one recipe was in force and glass technology was in a transitional phase (Towle and Henderson, 2007: 60). Data from analyses of glassy materials of objects discovered in Poland have confirmed this assumption, demonstrating the highly variable compositions of the analyzed glasses. Glass forming glassy faience (LMMK, LMG_{GF}) and true glass (LMG) differ in the contents of major and trace elements. Different raw materials were used for glass production and no consistent proportions and sources of the raw materials were imposed. LMMK glass was melted using sand (containing feldspar among others) and a flux (plant ash?) that is difficult to identify, whereas LMG_{GF} and LMG glass used sand (with less impurities) and natron. Glassy faience is usually blue and was colored with cobalt compounds. The yellow glass of the decoration was colored with lead antimonate.

It also appears that the same workshops formed objects made of materials produced using different recipes. One indication of this is the beads made of glassy faience that were decorated with true glass. It should also be noted that the pin heads from Domasław are formally identical, of the same color and decorated in identical fashion, but the glass of one of them is LMMK, while the other one represents LMG_{GF}. Thus, it seems obvious that these unique pieces were fashioned in the same workshop, but from a glassy faience that was made from different raw materials.

Acknowledgments

The authors would like to thank the following for making finds from their excavations available for laboratory analyses: Prof. Bogusław Gediga (Institute of Archeology and Ethnology, Polish Academy of Sciences, Wrocław), Monika Michnik (Museum in Gliwice), Prof. Marzena Szmyt and Tomasz Skorupka (Archaeological Museum in Poznań), Prof. Jan Chochorowski and Karol Dzięgielewski (Institute of Archeology, Jagiellonian University in Kraków), Dr. Renata Abłamowicz (Silesian Museum in Katowice), Bartłomiej Konieczny (Kraków Unit for Motorway Research). Special thanks are extended to Prof. Maria Dekówna (Institute of Archeology and Ethnology, Polish Academy of Sciences, Warsaw) for comments that have helped to shape the final version of this study.

Analyses of glass chemical composition were conducted within the framework of Research Grant N N109 202138 from the Ministry of Science and Higher Education of the Republic of Poland. The majority of those studies were carried out at the Biological and Chemical Research Centre, University of Warsaw, established within the project co-financed by European Union from the European Regional Development Fund under the Operational Programme Innovative Economy, 2007–2013.

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